P. 481

Adv. Q.M. (Bethe)

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Physics 481 — Advanced Quantum Mechanics.

Prof. Bethe Rockefeller Hall Room 1?4

Topics to be covered:

Matrix Mechanics
- Oscillator
- Angular Momentum
- Transition Probabilities (see in Condon & Shortley)

Transformation Theory

Group Theory — complex Spectra. Wigner, von Neumann 1927-29
- Slater, Hund, Pauli no group thy. 1930 32
- Then appl. to crystals
- also to nuclear physics, Wigner

Relativistic Wave Eqn, Dirac.

Radiation theory, & Quantum Electrodynamics.

Books recommended:

Rojansky — esp on Matrix Mech.

Kramers (Hand- & Jahrbuch d. chemischen Physik 1)
- esp. on Transformation theory.
- and on adiabatic perturbations.

Wigner — on group theory

Dirac — esp on Relat. Wave Eq.

Pauli - Handbuch $\overline{XXIV}$-1 - cap. on Dirac eqn,
and on radiation + quantum electrodynamics

Fermi. - R.M.P. on radiation

I Matrix Mechanics.

Consider a transformation changing a point x to a point y.
then the coordinates y_i are functions of the x_i;

$$\left.\begin{aligned} y_1 &= \sum_1^3 a_{1i} x_i \\ y_2 &: \cdots \\ y_3 &: \cdots \end{aligned}\right\} \text{ or } y = Ax$$

matrix of transformation : $\begin{pmatrix} a_{11} & a_{12} & \cdot \\ \cdot & a_{22} & \\ \cdot & \cdot & a_{33} \end{pmatrix} \equiv A$.

suppose also $z = By$;

then $z = BAx$

$$z_i = \sum b_{ij} y_j = \sum b_{ij} \sum a_{jk} x_k$$

$$= \sum c_{ik} x_k$$

matrix multiplication ⟶ where $c_{ik} = \sum_j b_{ij} a_{jk}$

$z = Cx$, $C = BA$.

in general $AB \neq BA$. non-commutative -

but distribution law holds: $A(BC) = (AB)C$.

and $A(B+C) = AB + AC$.

Rotation of space: vectors y & x have same length:

$|y| = |x|$ -

or $\sum y_i^2 = \sum x_i^2$

Therefore must have:

$$\sum y_i^2 = \sum x_i^2$$

$$\sum_i \left(\sum_j a_{ij} x_j\right)^2 = \sum x_i^2$$

$$\sum_{ikl} a_{ik} a_{il} x_k x_l = \sum x_i^2$$

$$\therefore \sum a_{ik} a_{il} = \delta_{kl}$$ orthogonality normalization

Define $\tilde{A}$, transposed matrix

$$\tilde{A}_{ij} = A_{ji}$$

$$\therefore \sum a_{ik} \tilde{a}_{li} = \delta_{kl}$$

$$\text{or } (\tilde{A} A)_{kl} = \delta_{kl} = 1$$

$$\therefore \tilde{A} A = 1 \quad \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Unitary ~~transformation~~

If $x_1\, x_2\, x_3$ are complex:

$$|x|^2 = \sum x_i x_i^*$$

a's are complex;

rotation: $\sum |y_i|^2 = \sum_i \left(\sum_k a_{ik} x_k\right)\left(\sum a_{il}^* x_l^*\right) = \sum |x|$

$$\therefore \sum a_{ik} a_{il}^* = \delta_{kl}$$

Define A^*: $(A^*)_{ij} = a_{ij}^*$

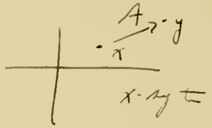
$\tilde{A}^*$: conjugate transpose. $\therefore \tilde{A}^* A = 1$

Unitary Matrix ≡ rotation of space

$$\tilde{A}^* A = 1$$

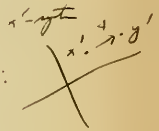
can also ~~rotate coordinates~~ instead of rotating space : also represented by unitary matrix

Consider a mapping A :



$y = Ax$

" same mapping in a different coord. system :



$$x' = Sx$$
$$y' = Sy$$
$$\therefore y' = SAx$$

Now introduce inverse matrix S^{-1} : $SS^{-1} = 1$, $S^{-1}S = 1$

For a unitary matrix : $S^{-1} = \tilde{S}^*$

$$\therefore \quad S^{-1}x' = S^{-1}Sx = x$$
$$\therefore y' = SAx = SAS^{-1}x'$$
$$\therefore y' = A'x', \quad A' = SAS^{-1}$$

also $S^{-1}A'S = S^{-1}SAS^{-1}S = A$

$\therefore A = S^{-1}A'S$

Can we diagonalize A? → ~~$A = \varepsilon I$~~ ~~$A - \varepsilon I = 0$~~ ?

$y = Ax = \varepsilon x$

$(A - \varepsilon I)x = 0$

only soluble if $|A - \varepsilon I| = 0$

or $\begin{vmatrix} a_{11}-\varepsilon & a_{12} & a_{13} \\ a_{21} & a_{22}-\varepsilon & a_{23} \\ a_{31} & a_{32} & a_{33}-\varepsilon \end{vmatrix} = 0$ can find 3 ε's

which will transform A to principal axes – three

direction along which there is only compression or expansion.

Ratio $x_1 : x_2 : x_3$ given

If $x_1 : x_2 : x_3 = \alpha : \beta : \gamma$, then $y_1 : y_2 : y_3 = \alpha : \beta : \gamma$

$$y = \varepsilon x$$

Then transform to principal system: $A' = \begin{pmatrix} \varepsilon^{(1)} & 0 & 0 \\ 0 & \varepsilon^{(2)} & 0 \\ 0 & 0 & \varepsilon^{(3)} \end{pmatrix}$

where $\varepsilon^{(1)(2)(3)}$ are roots of $|A - \varepsilon I| = 0$

Now to Quantum Mech.

Operate on a $\psi(x, t)$ with A: $A\psi$

A ~~contains~~ $A = A(x, \frac{\partial}{\partial x} \cdots)$ (not time)

Suppose ψ is n^{th} eigenf'n of some dynamical problem $\psi_n = u_n(x) e^{-\frac{i}{\hbar} \ldots}$

then $A\psi_n$ is not in general an eigenf'n.

But if we know all the eigenf'ns, we can expand in terms of them:

$$A u_n = \sum_m a_{nm} u_m \quad \left(+ \int a_n(m) u(m) dm \right) \text{ if cont. spectrum}$$

$$a_{nm} = \int u_m^* A u_n \, dx \text{, since } u_n \text{ are orthonormal}$$

Suppose $\psi_{\cancel{nt}} = \sum_n c_n \psi_n = \sum b_n u_n e^{\sim}$

$$A\psi = \sum_n b_n \sum_m a_{nm} u_m = \sum \bar{b}_m u_m$$

then $\bar{b}_m = \sum_n a_{nm} b_n$

just like $y_i = \sum a_{ij} x_j$

∴ b's are analogous to coordinates in ordinary space;

a f'n ψ can be represented by its "coordinates" b_n

"Hilbert space" — infinite no. of dimensions; each axis corresp. to a quantum state (mathematically, to one of the characteristic f'ns of an orthonormal set)

Any wave f'n ψ is represented by a pt. in Hilbert space.

Any operation A corresponds to a mapping in Hilbert space.

$$b_n = c_n e^{-\frac{i}{\hbar}E_n t} \qquad A\psi = \sum \bar{c}_m \psi_m$$

introduce $\bar{c}_m = \bar{b}_m e^{\frac{i}{\hbar}E_m t}$

$$\bar{c}_m = \sum_n a_{nm} e^{\frac{i}{\hbar}(E_n - E_m)t} c_n$$

$$= \sum_n A_{nm} c_n \qquad A_{nm} = a_{nm} e^{\frac{i}{\hbar}(E_n - E_m \ldots}$$

(sometimes use time-dependent, sometimes time-independent coeffi...

10/1/40 operator A : wave f'n ψ :

can expand ψ and $A\psi$ in terms of eigen f'n's.

$$A\psi = \sum_n b_n \psi_n \qquad \psi = \sum_n c_n \psi_n$$

$$b_n = \sum_m a_{mn} c_m \qquad a_{mn} = \int \psi_n^* A \psi_m$$

if $A = A(x)$ and real, ~~A~~ $a_{nm} = a_{mn}^*$. Hermitean matrix

$$\tilde{A}^* = A. \qquad (\text{Unitary}: \tilde{A}^* = A^{-1}$$

if $A = A(p)$ and real

(1) $A = p = -i\hbar \frac{\partial}{\partial x}$; $p_{mn} = -i\hbar \int \psi_n^* \frac{\partial \psi_m}{\partial x} = +i\hbar \int \frac{\partial \psi_n^*}{\partial x} \psi_m$

$$p_{nm} = -i\hbar \int \psi_m^* \frac{\partial \psi_n}{\partial x} = p_{mn}^* \quad \therefore p \text{ is Hermit...}$$

consider two operators A & B: $AB\psi = \sum_n d_n \psi_n$

~~$A \quad d_n = \sum_m (AB)_{mn} c_m$~~

~~$= \sum_m \sum_j a_{mj} b_{jn} c_m$~~

Hereafter $A_{nm} = \int \psi_n^* A \psi_m$

etc.

$AB\psi = \sum d_n \psi_n$; $(AB)_{nm} = \int \psi_n^* AB \psi_m$

$B\psi_m = \sum_l b_{ml} \psi_l$

$= \int \psi_n^* A \sum_l b_{ml} \psi_l$

$= \sum_l b_{ml} \int \psi_n^* A \psi_l = \sum b_{ml} a_{nl}$

$= \sum_l b_{ml} \int (\psi_n)^* \sum = \sum_l a_{nl} b_{lm}$

∴ Matrices representing wave ; mech.

Operators follow laws of matrix algebra.

Matrix of p is Hermitean ; hence also p^2 ;

for $p^2_{mn} = \sum_l p_{ml} p_{ln} = \sum_l p_{lm}^* p_{nl}^* =$

$p^2_{nm} = \sum_l p_{nl} p_{lm} = (p^2_{mn})^*$

likewise p^r is Hermitean ;

Hence any power-series-representable function is Hermitean

Hence all ordinary f^ns of x & p are Hermitean

~~also $f(x) g(p)$ is Hermitean~~ ;

∴ any real function of x's & p's is represented by a Hermitean

Matrix ?

Commutation

in general $AB \neq BA$.

e.g. $[px - xp] = -i\hbar\left[\frac{\partial}{\partial x}x - x\frac{\partial}{\partial x}\right] = -i\hbar\left[x\frac{\partial}{\partial x} + 1 - x\frac{\partial}{\partial x}\right]$

$= -i\hbar$.

commutator is diagonal; in fact $i\hbar 1$.

flashback: if A + B are hermitian, $(AB)_{mn} = \sum_l a_{ml} b_{ln}$

$(AB)^*_{mn} = \sum_l a^*_{ml} b^*_{ln} = \sum a_{lm} b_{nl}$

$= (BA)_{nl}$

$\therefore \widetilde{AB}^* = BA$

$\therefore$ AB in general not Hermitean

$\therefore$ xp not Hermitean,

for $\widetilde{xp}^* = px \neq xp$.

but $\widetilde{(xp+px)}^* = (px+xp) = xp+px$, $\therefore$ Hermitean

$\therefore$ if A + B are Hermitean,

$\frac{1}{2}(AB+BA)$ is Hermitean.

"symmetrized product".

Used to be important to "symmetrize" the Hamiltonian

Since Hamiltonian must be Hermitean.

[only Hermitean operators have real eigenvalues].

(can be shown that roots ε of $\|A - \varepsilon 1\| = 0$

are real only if $A_{nm} = A^*_{mn}$.]

All dynamical quantities must be represented by Hermitean operators

find comm. of $x^2 p^2$

Oct 3 $\quad px - xp = -i\hbar$

(for corresponding coörds & mom.)

or: $\quad p_k x_l - x_l p_k = -i\hbar\, \delta_{kl}$ $\qquad k, l = 1, \dots 3n$ for n particles

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$$[p^2 x] = p[px] + [px]p = -2i\hbar p$$

$$[p^n x] = p^{n-1}[px] + [p^{n-1} x]p = -i\hbar p^{n-1} + [p^{n-1} x]p$$

$$\downarrow$$

$$(i\hbar p^{n-2} + [p^{n-2} x]p)p$$

$$\downarrow$$

$$i\hbar p^{n-1} + [p^{n-2}, x]p^2$$

$$\therefore \; [p^n x] = -i\hbar n p^{n-1}$$

$$[f(p)\, x] = -i\hbar \frac{df}{dp}.$$

$$[p x^n] = -i\hbar n x^{n-1}$$

$$[p\, f(x)] = -i\hbar \frac{\partial f}{\partial x}.$$

$$[p^2 x^2] = p[px^2] + [px^2]p\,x = -2i\hbar[px + xp]$$

$$[p^m x^n] = -ni\hbar[p^{m-1}x^{n-1} + p^{m-2}x^{n-1}p + \dots + x^{n-1}p^{m-1}]$$

$$[f(p)g(x)] = -i\hbar\left[S \frac{df}{dp}\frac{dg}{dx}.\right]$$

where S indicates symmetrized expression

$$H_{mn} = \int \psi_m^* H \psi_n = E_n \delta_{mn}$$

Suppose we have a matrix A: calculate $(AH - HA)$

$$(AH - HA)_{mn} = (AH)_{mn} - (HA)_{mn} = \sum_l A_{ml} H_{ln} - \sum_l H_{ml} A_{ln}$$

$$= A_{mn} E_n - E_m A_{mn}$$

$$= A_{mn}(E_n - E_m)$$

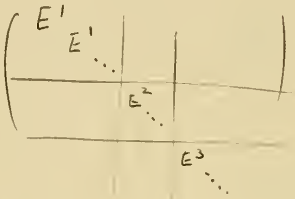
If A is also diagonal : $A_{mn} = A_n \delta_{mn}$

$$(AH - HA)_{mn} = (E_n - E_m) A_{mn} = (E_n - E_m) A_m \delta_{mn} \equiv 0 .$$

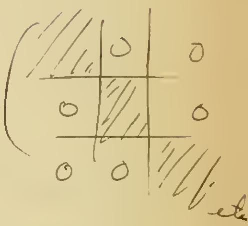
Two diagonal matrices commute.

A diagonal matrix H commutes ~~with~~ a matrix A if A_{mn} vanishes for states for which $E_m \neq E_n$

e.g.: if $H =$



$A =$



A ~~commutes~~ with H if $A_{mn} \neq 0$ only in squares.

Now $A_{mn} = \int \psi_m^* A \psi_n = \int u_m^* A u_n \, e^{\frac{it}{\hbar}(E_m - E_n)} = \alpha_{mn} e^{\frac{it}{\hbar}(E_m - E_n)}$

α_{mn} independent of t

Now $\dfrac{dA_{mn}}{dt} = \dfrac{i}{\hbar}(E_m - E_n) A_{mn} = -\dfrac{i}{\hbar}(AH - HA)_{mn}$

$$\therefore \quad \frac{dA}{dt} = -\frac{i}{\hbar}(AH - HA) = -\frac{i}{\hbar}[AH] .$$

if $A = H$, $\dfrac{dH}{dt} = 0$

suppose $\psi = \sum c_n \psi_n$

then $\text{av}\, A = \int \psi^* A \psi = \int \sum c_m^* \psi_m^* A \sum c_n \psi_n = \sum_{m,n} c_m^* c_n A_{mn}$

$$\text{av} \frac{dA}{dt} = \sum_{mn} c_m^* c_n \frac{dA_{mn}}{dt}$$

$$\frac{dx}{dt} = -\frac{i}{\hbar}[x H] \qquad H = H(x, p).$$

$$= V(x) + T(p) \quad \text{in simple cases.}$$

$$\therefore \frac{dx}{dt} = -\frac{i}{\hbar}[x, T(p)] = -\frac{i}{\hbar}\cdot i\hbar\frac{dT}{dp} = \frac{dT}{dp} = \frac{\partial H}{\partial p}$$

$$\dot{x} = \frac{\partial H}{\partial p}.$$

$$\frac{dp}{dt} = -\frac{i}{\hbar}[p H] = -\frac{i}{\hbar}[p. V] = -\frac{i}{\hbar}\cdot -i\hbar\frac{\partial V}{\partial x} = -\frac{\partial V}{\partial x} = -\frac{\partial H}{\partial x}$$

$$\therefore \dot{p} = -\frac{\partial H}{\partial x}$$

which are the classical ~~Hamiltonian~~ Hamilton eq'n's. !

Hence in Q.M., $\frac{dA}{dt} = -\frac{i}{\hbar}[A H]$ is called eq'n of ~~motion~~ motion.

Derive Ham. eqns from Schroedinger eq'n.

10/5/40 $[p, x] = -i\hbar$

$$\frac{dA}{dt} = -\frac{i}{\hbar}[A, H], \text{ whence } \begin{cases} \frac{\partial x}{\partial t} = \frac{\partial H}{\partial p} \\ \frac{\partial p}{\partial t} = -\frac{\partial H}{\partial x} \end{cases}$$

center of gravity of wave packet moves according to Ham. Eq., i.e. class. mech.

Transition to classical mechanics.

Classical Mechanics applicable if a wave packet can be constructed over which the force does not vary appreciably.

Extension of wavepacket: $\frac{\lambda_p}{\Delta p} = \frac{\hbar}{\Delta p}$

Variation of force over one wave length must be small.

Bohr correspondence principle: in limit of high quantum no's, can use classical mechanics; in particular, can calculate radiation.

For high q.n.'s, get nearly equidistant energy levels:

$$x_{mn} = x^0_{mn}\, e^{\frac{it}{\hbar}(E_m - E_n)}$$

for equidistant levels: $x_{mn} = x^0_{mn}\, e^{\frac{it}{\hbar}\frac{dE}{dn}(m-n)}$

$$= x^0_{mn}\, e^{i\omega_0 t(m-n)}$$

$$\psi = \sum c_n \psi_n$$

suppose we construct a ψ with concentration of ψ_n's about n.
it will be about at the n's orbit in Bohr theory.

higher x_{mn}'s correspond to classical Fourier components of x, from which radiation, etc. are calculated. : emitted radiation $\sim |x_{mn}|^2 \omega$

$\omega = \omega_0(m-n)$

Heisenberg devised a scheme which gave correspondence between high q.n.'s & classical mech.

Derived commutation relation so as to give quantum condition

Transition probabilities — $nl \to n'l'$ strong if n, l change in same direction
weak " " " " opposite "

if $l \approx n$, trans. prob. for large Δn is very small.
if $l \ll n$, " " decreases slowly with inc. Δn

[if $l \approx n$, almost circular orbit; then coord. x is nearly $\sin$, ~~[illegible]~~ & Fourier coeff of all but ω_0 vanish; but eccentric orbit will contain many

Harmonic oscillator by Matrix mechanics.

$$H = p^2/2m + \frac{m\omega^2}{2}x^2$$

$$\dot{x} = \frac{\partial H}{\partial p} = p/m \qquad \therefore\ m\dot{x}_{mn} = p_{mn}$$

$$\dot{p} = -\frac{\partial H}{\partial x} = -m\omega^2 x \qquad \dot{p}_{mn} = -m\omega^2 x_{mn}$$

$$[\ \ddot{p}_{mn} = -\omega^2 p_{mn},$$

$$p_{mn} = m\dot{x}_{mn} = m\cdot -\frac{i}{\hbar}\left[xH - Hx\right]_{mn} \qquad \ddot{x}_{mn} = -\omega^2 x_{mn}$$

$$= -\frac{im}{\hbar}x_{mn}\left[E_n - E_m\right] \qquad x_{mn} = -\frac{1}{m\omega^2}\dot{p}_{mn} = +\frac{i}{m\omega^2\hbar}\left[pH - Hp\right]$$

$$= \frac{i}{m\omega^2\hbar}p_{mn}(E_n - \ldots$$

$$\therefore\ p_{mn} = -\frac{im}{\hbar}\left[E_n - E_m\right]\frac{i}{m\omega^2\hbar}p_{mn}(E_n - E_m) = \frac{1}{\omega^2\hbar^2}(E_n - E_m)\ldots$$

and
$$x_{mn} = \frac{i}{m\omega^2\hbar}(E_n - E_m)\left(-\frac{im}{\hbar}(E_n - E_m)x_{mn} = \frac{1}{\omega^2\hbar^2}(E_n - E_m)\ldots\right.$$

$\therefore\ x_{mn}, p_{mn}, \neq 0$ only if $(E_n - E_m)^2 = \hbar^2\omega^2$

$$E_n - E_m = \pm\hbar\omega$$

otherwise, $x_{mn} = 0$.

$\therefore$ matrix elements exist only between states whose energy difference is $\pm\hbar\omega$.

Oct. 8] Physics

$$\therefore\ x_{mn} = x^0_{mn}\, e^{i/\hbar (E_n - E_m)t} = x^0_{mn}\, e^{\pm i\omega t}$$

$\therefore$ all matrix elements have classical vibration freq

If there is a level E_n, ~~then are~~ levels $E_n \pm \omega\hbar$; hence $E_n \pm 2\ldots$ etc

$\therefore$ levels are given by $E_n = \hbar\omega(\alpha + n)$ $\quad\alpha$ a constant

(so far, might have several α's, hence several series).

Now calculate energy matrix elements.

$$E_n = H_{nn} \qquad H_{mn} = \frac{1}{2m}\sum_l p_{ml} p_{ln} + \frac{1}{2} m\omega^2 \sum_l x_{ml} x_{ln}$$

~~$= \frac{1}{2m} p_{nn}$ ~~ ~~Σ 0 unless~~

$= 0$ unless $m = n$.

~~$= \frac{1}{2m} p_{nn}$~~

$$E_n = H_{nn} = \frac{1}{2m}\left(p_{n,n+1} p_{n+1\,n} + p_{n\,n-1} p_{n-1\,n}\right)$$

$$+ \frac{1}{2} m\omega^2 \left(x_{n,n+1} x_{n+1,n} + x_{n,n-1} x_{n-1,n}\right)$$

$$= \frac{m}{2\hbar^2}(E_n - E_l)^2 x_{nl} x_{ln} + \frac{1}{2} m\omega^2 x_{nl} x_{ln}$$

$$= \left(\frac{1}{2} m\omega^2 + \frac{1}{2} m\omega^2\right) \sum_l x_{nl} x_{ln}$$

$$= m\omega^2 \sum x_{nl} x_{nl}^{\dagger} \qquad \text{(since } x \text{ is Hermitian)}$$

$$= m\omega^2 \left[|x_{n,n-1}|^2 + |x_{n,n+1}|^2 \right]$$

$$= \hbar\omega(\alpha + n)$$

$$\therefore \; |x_{n,n-1}|^2 + |x_{n\,n+1}|^2 = \frac{\hbar}{m\omega}(n + \alpha)$$

also $$|x_{n+1,n}|^2 + |x_{n+1,n+1}|^2 = \frac{\hbar}{m\omega}(n + 1 + \alpha)$$

$$\therefore \; |x_{n+2,n+1}|^2 - |x_{n,n-1}|^2 = \frac{\hbar}{m\omega}$$

$$\therefore \; |x_{n-1,n}|^2 = \frac{\hbar}{2m\omega}(n + \beta)$$

$$\therefore \; \frac{\hbar}{2m\omega}\left((n+\beta) + (n+1+\beta)\right) = \frac{\hbar}{m\omega}(n + \alpha)$$

$$\therefore \; n + \beta + \tfrac{1}{2} = n + \alpha;$$

$$\therefore \; \alpha = \beta + \tfrac{1}{2}$$

Now $|x_{\ldots}|^2$ must not be negative; hence there

must be a smallest value of n for which the matrix element exists. ; Hence there must be a smallest energy level E_0. Hence there exists no $|x_{0,-1}|$;

$$\therefore \quad |x_{0,1}|^2 = \frac{\hbar}{m\omega}\alpha ;$$

$$\text{also} \quad |x_{-1,0}|^2 = 0 = \frac{\hbar}{2m\omega}(\alpha+\beta)$$

$$\therefore \beta = 0, \quad \alpha = \tfrac{1}{2}$$

$$\text{and } E_n = \omega\hbar(n+\tfrac{1}{2}) \qquad n = 0, 1, \dots$$

$$x_{n-1,n} = \sqrt{\frac{\hbar n}{2m\omega}}\, e^{i\gamma_n}$$

γ_n is arbitrary (just as in wave mech. each wave fn is arbitrary to a phase factor).

This theory gives all that Schroedinger theory gives — energy levels, matrix elements.— in a shorter way. But as soon as ~~Hamiltonian~~ becomes more complicated, matrix mechanics

$$E = \begin{pmatrix} \tfrac{1}{2} & & & 0 \\ & \tfrac{3}{2} & & \\ & & \tfrac{5}{2} & \\ 0 & & & \ddots \end{pmatrix} \hbar\omega \qquad x = \begin{pmatrix} 0 & 1 & & & \\ 1 & 0 & \sqrt{2} & & \\ & \sqrt{2} & 0 & \sqrt{3} & \\ & & \sqrt{3} & 0 & \sqrt{4} \\ & & & \sqrt{4} & 0 & \ddots \\ & & & & \ddots & \ddots \end{pmatrix} \sqrt{\frac{\hbar}{2m\omega}} \quad (\gamma_n = 0)$$

$$p = \begin{pmatrix} 0 & -i & & & \\ i & 0 & -i\sqrt{2} & & \\ & i\sqrt{2} & 0 & -i\sqrt{3} & \\ & & i\sqrt{3} & 0 & -i\sqrt{4} \\ & & & i\sqrt{4} & 0 & \ddots \\ & & & & \ddots & \ddots \end{pmatrix} \sqrt{\tfrac{1}{2}\hbar m\omega}$$

$x^2 + p^2$ have elements in main diagonal and 2nd diagonal away: the main diagonals add, + the subtract, to make E diagonal

Angular Momentum.

(… particle).

$$\underline{M} = \underline{r} \times \underline{p}$$

$$M_3 = x p_y - y p_x \text{, etc.}$$

$$[z, M_3] = 0 = [p_3 M_3]$$

$$[x M_3] = [x\, x p_y] - [x\, y p_x] = x[x p_y] + [x p_y]x - x[y p_x] - [x p_x]y$$

$$= -i\hbar y.$$

$$[z M_x] = i\hbar y \qquad \text{etc.}$$

$$[p_x M_3] = [p_x x] p_y = -i\hbar p_y.$$

$$[p_3 M_x] = i\hbar y \quad \text{etc.}$$

$$[r^2 M_3] = [x^2 + y^2 + z^2, M_3]$$

$$= [x^2, M_3] + [y^2, M_3]$$

$$= x[x M_3] + [x M_3]x + y[y M_3] + [y M_3]y$$

$$= -2i\hbar xy + 2i\hbar xy = 0.$$

also $[f(r^2), \underline{M}] = 0$

$$[f(p^2), \underline{M}] = 0$$

$[f(q), \underline{M}] = 0$

$[g(p), \underline{M}] = 0$

$[H(p,q), \underline{M}] = 0$ if $H(p,q) = T(p) + V(q)$

∴ M has matrix elements only between states of same energy.

true for $M_{x,y,z}$, $M^2_{x,y,z}$ also for M^2

Matrix of M^2 can be diagonalized by taking appropriate linear combinations of ψ's. If a matrix B commutes with a diagonal matrix A, B can also be diagonalised by taking suitable linear comb.'s of ψ's belonging to one eigenvalue of A. ?

$$[M_z, M_x] = [M_z, y p_z - z p_y] = [M_z, y p_z] - [M_z, z p_y]$$

$$= y[M_z p_z] + [M_z, y] p_z - z[M_z p_y] - [M_z, z] p_y$$

$$= -i\hbar [x p_z - z p_x]$$

$$= -i\hbar M_y \quad \text{etc.}$$

$$\underline{M} \times \underline{M} = -i\hbar \underline{M}$$

also $[\underline{M}, M^2] = 0$.

Suppose each state corresponds to a definite value of E & M^2.

then $M_{x,y,z}$ have matrix elements only between states of the same E & M^2.

Suppose M_3 is also diagonal.
(then M_x & M_y can not be diagonalized)

~~$[M_x, M_y]_{mn} =$~~

$$[M_3, M_x]_{mn} = (M_{3;m} - M_{3;n}) M_{x;mn} = i\hbar M_{y;mn}$$

$$[M_3, M_y]_{mn} = (M_{3;m} - M_{3;n}) M_{y;mn} = -i\hbar M_{x;mn}$$

$$\therefore (M_{3;m} - M_{3;n})^2 M_{x;mn} = \hbar^2 M_{x,mn}$$

$$\therefore M_{x;mn} \neq 0 \text{ only if } M_{3;m} - M_{3;n} = \pm\hbar$$

$\therefore$ eigenvalues : $M_{3;m} = \hbar(m + \alpha)$

$$M_{y;m(m+1)}(-\hbar) = -i\hbar M_{x;m(m+1)}$$
$$M_{y;m(m-1)}(\hbar) = i\hbar M_{x;m(m-1)}$$

$$\therefore (M_y - iM_x)_{m,m+1} = 0$$
$$(M_y + iM_x)_{m,m-1} = 0$$

$$[M_x M_y]_{mm} = M_{x;m,m+1} M_{y;m+1,m} + M_{x;m,m-1} M_{y;m-1,m}$$
$$- M_{y;m,m+1} M_{x;m+1,m} - M_{y;m,m-1} M_{x;m-1,m}$$

$$= -i M_{x;m,m+1} M_{x;m+1,m} + i M_{x;m,m-1} M_{x;m-1,m}$$

$$- i M_{x;m,m+1} M_{x;m+1,m} + i M_{x;m,m-1} M_{x;m-1,m}$$

$$= 2i M_{x;m,m-1} M_{x;m-1,m} - 2i M_{x;m,m+1} M_{x;m+1,m}$$

Since M's are Hermitian matrices:

$$[M_x M_y]_{mm} = 2i\left\{ |M_{x;\,m-1,m}|^2 - |M_{x;\,m,m+1}|^2 \right\}$$

but $[M_x M_y]_{mm} = i\hbar M_{z;\,mm} = i\hbar(m\hbar)$ (m might be fraction)

$$= i\hbar^2 m$$

$$\therefore |M_{x;\,m-1,m}|^2 - |M_{x;\,m,m+1}|^2 = \frac{m\hbar^2}{2}$$

$$\therefore |M_{x;\,m,m+1}|^2 = \hbar^2(\alpha + \beta m + \gamma m^2)$$

$$|M_{x;\,m-1,m}|^2 = \hbar^2(\alpha + \beta(m-1) + \gamma(m^2 - 2m + 1))$$

$$\text{diff.} = \hbar^2\{-\beta - 2\gamma m + \gamma\} = m\frac{\hbar^2}{2}$$

$$\therefore \beta = \gamma; \quad -2\gamma = \tfrac{1}{2}$$

$$\gamma = -\tfrac{1}{4}$$

$$|M_{x;\,m,m+1}|^2 = \hbar^2\left(\alpha - \tfrac{1}{4}m - \tfrac{1}{4}m^2\right)$$

$$= \frac{\hbar^2}{4}\left(\alpha' - m(m+1)\right)$$

$$(M^2)_{mm} = M^2_{x;\,mm} + \dots$$

$$= M_{x;\,m,m+1} M_{x;\,m+1,m} + M_{x;\,m,m-1} M_{x;\,m-1,m} + (y) + (3)$$

but $M^2_{z\,mm} =$

$$= \frac{\hbar^2}{4}\left(\alpha' - (m)(m+1) + \alpha' - m(m-1)\right) + \text{same} + m^2\hbar^2$$

$$= \hbar^2\left(\alpha' - m^2 + m^2 - m\tfrac{1}{2}m\right) = \alpha''\hbar^2$$

Suppose last existing state has $m = l$; then $M_{x;\,l,l+1} = 0$, $\alpha' = l(l+1)$

then $M_x = 0$ also when $m = -l-1$

m goes from $-l$ to $+l$

and $M^2 = \hbar^2\, l(l+1)$.

Oct 12

~~Eigenvalues~~ of M^2 : $l(l+1)\hbar^2$

M_3 : $m\hbar = -l, -l+1, \dots, l-1, l \cdot \hbar$ $2l+1$ values of m

matrix elements of M_x exist only between states of same l, m diff by 1

l may be integral or half-integral. since $2l+1 = n$

By considering $xp_y - yp_x$, etc. can show that for orbital momentum, l must be integral (cf. Dirac).

[in wave mech, l is order of sph. harm., which must be integral if sph. harm. is single valued]

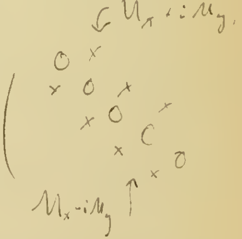
Notice that if $M_3 = \pm l$, $M_3^2 = l^2$; but $M^2 = l(l+1)$;
(hence $M_x^2 + M_y^2 = \hbar^2 l$).

so simple vector model is dangerous.

We found $M_{x,m,m+1} = \frac{\hbar}{2}\sqrt{l(l+1) - m(m+1)}$

or $\sqrt{(l-m)(l+m+1)}$

Often convenient to use: $M_x \pm i M_y$

these have elements: 

(These are Non-Hermitian operators)

(using usual sph. harm's, $M_{x:m,m+1}$ has negative sign!)

(ii) Many-electron, cont. —

Potential energy V contains terms $f(r_i)$ $g(r_{ik})$.

$[\underline{M}_i, r_i] = 0$

also $[M_i, r_k] = 0$

But $[\underline{M}_{xi}, r_{ik}^2] = [M_{xi}, (x_i - x_k)^2 + \cdots\cdots]$

$= 0 + [M_{xi} (y_i - y_k)^2] + [M_{xi} (z_i - z_k)^2]$

$= -2[M_{xi}, y_i y_k] - 2[M_{xi}, z_i z_k]$.

$= -2[i\hbar z_i y_k - i\hbar y_i z_k]$

$= +2i\hbar[y_i z_k - z_i y_k]$

or : $[\underline{M}_i, r_{ik}^2] = 2i\hbar\, \underline{r}_i \times \underline{r}_k$

also $[\underline{M}_k, r_{ik}^2] = 2i\hbar\, \underline{r}_k \times \underline{r}_i$.

Hence $[\underline{M}_i + \underline{M}_k, r_{ik}^2] = 0$!

Hence sum of moments of a pair of electrons commutes with relative position vector, & functions of it.

Also total orbital momentum $\underline{M} = \sum_k \underline{M}_k$ commutes with Hamiltonian (i.e. with all electron interactions).

$[M_x, M_y] = i\hbar M_3$, etc.

Total mom. has same com. relations as single one.

$\therefore\ M^2 = \hbar^2 (L+1) L$ M, L, integers.

$M_3 = \hbar M$. $M = -L \cdots\cdots L$

Spin.

Pauli — correct to terms v^2/c^2.

1st approximation to Dirac eqn.

Each electron has intrinsic angular momentum: quantum no. ½.

Components of spin $S_{x,y,z}$; $S_x S_y - S_y S_x = i\hbar S_z$ etc. just like any mom.

$$[S_{x,y,z}, S^2] = 0$$

$$[S_{x,y,z}, f(r)\,g(p)] = 0.$$

Spin depends on new coordinate.

$$S^2 = \hbar^2 (s)(s+1)$$

$$S_z = \hbar\mu, \quad \mu = -s, \dots +s.$$

For one electron: experimentally, $s = \frac{1}{2}$ (always).

$\therefore S_z = -\frac{1}{2}, \frac{1}{2}$;

$$\therefore \quad S_z = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix} \hbar$$

$$S_{x:\mu;\mu+1} = \tfrac{1}{2}\hbar\sqrt{(s-\mu)(s+\mu+1)} = \begin{cases} \frac{1}{2}\hbar, & \mu = -\frac{1}{2} \end{cases}$$

$$\therefore S_x = \hbar \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix}$$

also $S_y = \hbar \begin{pmatrix} 0 & -\frac{1}{2}i \\ \frac{1}{2}i & \end{pmatrix}$.

use ~~instead~~ Pauli matrices: $\sigma = \dfrac{S}{\hbar/2}$.

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Show $[S_x S_y] = i\hbar S_z$
find S^2;

Interaction of spin & orbit.

assume $\sim f(r)\, \underline{M}\cdot\underline{S}$.

$$[M_x, \underline{M}\cdot\underline{S}] = [M_x, M_x S_x] + [M_x, M_y S_y] + [M_x, M_z S_z]$$

$$= [M_x, M_y] S_y + [M_x, M_z] S_z = i\hbar [M_z S_y - M_y S_z]$$

$= \neq$

also $[S_x, \underline{M}\cdot\underline{S}] = -i\hbar[M_3 S_1 - M_1 S_3]$.

$\therefore [M_x + S_x, M\cdot S] = 0$.

Prove: $[M^2, \underline{M}\cdot\underline{S}] = 0$

$\therefore$ also $[(\underline{M}+\underline{S})^2, \underline{M}\cdot\underline{S}] = 0$.

hence $[M^2 + S^2, M\cdot S] = 0$.

also $[M^2, M\cdot S] = 0$

$[S^2, M\cdot S] = 0$

$2\,M\cdot S = (M+S)^2 - M^2 - S^2$

everything said above about ang. mom. holds for $\underline{M}+\underline{S}$

$(M+S)^2 = \hbar^2 j(j+1)$

$\therefore 2\,M\cdot S = \hbar^2 [j(j+1) - l(l+1) - s(s+1)]$.

Can also ~~introduce~~ ~~total~~ ang. mom. of many electrons;

$J = \underline{M}+\underline{S} = \sum_k M_k + \sum_k S_k$

$[J, f(r_{ik})] = 0$

also $[J, M\cdot S] = 0$;

$\therefore J$ commutes with whole Hamiltonian & is a true quantum

Oct 15 Summary of ang. mom. results.

$[M_x T_x] = 0$ T_x, x comp. of coord, $\underline{r}$

mom. $\underline{p}$

$[M_x T_y] = i\hbar T_z$ ang. mom. $\underline{M}$

also if M is total ang mom of system, or T is r_i for i-th particle, or S_i for spin of i-th p

also:

$[\underline{M}, T_1 \cdot T_2] = 0$

for $[M_x, T_1 T_2] = [M_x, T_1] \cdot T_2 + T_1 [M_x, T_2]$

$= i\hbar \{ T_{1z} T_{2y} - T_{1y} T_{2z} + T_{1y} T_{2z} - T_{1z} T_{2y} \} = 0$

Scalar products like these occur in relativistic Hamiltonian.

M commutes with $L_i S_i$, with $r_i \cdot p_i$ for single electrons.

Opt. of ~~transition~~ for radiation polarized in z direction between two states m & n

is given by $z_{mn} = (m|z|n) = (E l m|z|E' l' m')$

electron rule | or for whole system: $(E J M|z|E' J' M')$

this vanishes for $M \neq M'$, since z commutes with M_z, which is diagonal.

$(E J M|\substack{x \\ y}|E' J M') \neq 0$ if $|M - M'| = 1$

Assume $J' = J$; then

$(E J M|[x M_z]|E' J M') = (E J M|x|E' J M')(M' - M)\hbar$

$= -i\hbar(\cdots|y|\cdots)$

For states of same J: $(E J M|x|E' J M') = \alpha_{J, EE'} (\not{E} J M|M_x|J M')$

$\alpha \cdots (\cdots M_z|\cdots)$

$|(\cdots|x|\cdots)|^2$ gives ~~intensity~~ of Zeeman component of line —

J selection rule

$$[M^2, z] = \sim\!\!\sim$$

$$[M^2, [M^2, z]] \text{ depends on } z + M_z \qquad \text{C. S.}$$

$$= M^4 z - 2M^2 z M^2 + z M^4$$

$$= 2\hbar^2 [M^2 z + z M^2 - 2 M_z \mathbf{M} \cdot \mathbf{r}]$$

Transitions $J \to J'$ possible –

$$(E J M | \cdots | E' J' M) = (\cdots|z|\cdots)\{J^2(J+1)^2 - 2J(J+1)J'(J'+1) + J'^2(J'+1)^2\} - 2\hbar^2(J(J+1) + J'(J'+1))$$

$$= - - \{[(J-J')^2-1][(J+J'+1)^2+1]\} = 0$$

$\therefore (-|z|-) \neq 0$ unless

$(J-J')^2 - 1 = 0$

or $J - J' = \pm 1$

Parity must change in dipole transition

Read Condon + Shortley !

Transformation Theory.

Problem: find wave function such that any given observable is represented by a diagonal matrix. These ~~matrix~~ wave f'ns will not have the same simple time dependence as previously —

Theory of transformations from one system of w f'ns to another, in which different observables are diagonal.

These transformations are a choice of new axes in Hilbert space.

Oct 17 | In three dimensions:

New coordinates of a vector after a mapping A:

$$y_m = \sum A_{mn} x_n \quad .$$

Then ask whether can find a new set of axes x' ~~such that~~

$$x_n = \sum S_{ni} x'_i$$

$$x = S x'$$

Define $S^{-1}S = 1$, then $S^{-1}x = x'$.

must have $\sum |x_n|^2 = \sum |x'_n|^2$;

from this, must have $S\tilde{S}^* = I$,

or $S^{-1} = \tilde{S}^*$.

Then $y_m = \sum S_{mk} y'_k = \sum_n \sum_i A_{mn} S_{ni} x'_i$

Now want to transform to principal axes — i.e. $y'_k = \lambda_k x'_k$

then equate coefficients: $S_{mk}\lambda_k = \sum_n A_{mn} S_{nk}$ for each k, m

This gives 9 equations for the nine S_{ij}'s.

solution if det. of coefficients vanishes: $\| A_{mn} - \lambda_k \delta_{mn} \| = 0$

This gives ratios of S_{ij}'s – normalize by unitary requirement $S\tilde{S}^* = 1$

$\sum_n |S_{nk}|^2 = 1 \qquad \sum S_{nk} S_{ni}^* = 0$ if $k \neq i$.

In Hilbert space:

coordinates are expansion coefficients of a ψ with respect to a set of eigenf'ns ψ_n.

$$\Psi = \sum_n c_n \psi_n.$$ c's like x's

Operator $$A\psi = \sum_n b_n \psi_n$$ b's like y's.

$$= \sum_n c_n A \psi_n$$

$$= \sum_n c_n \sum_m A_{mn} \psi_m$$

$$A_{mn} = \int \psi_m^* A \psi_n$$

where $$b_m = \sum_n A_{mn} c_n$$ A_{mn} like A_{mn}

Can we introduce a new system of axes? – (i.e. a new set of basic eigen f'ns) such that A is represented by a diagonal matrix?

Suppose we have a system of eigen f'ns ψ_n'.

Then $$\psi = \sum_n c_n' \psi_n'$$

$$c_m = \sum_n S_{mn} c_n'$$

$$\therefore \psi = \sum_m \sum_n S_{mn} c_n' \psi_m = \sum_n c_n' \psi_n'$$

$$\therefore \psi_n' = \sum_m S_{mn} \psi_m$$ & we know relation between ψ's

$$b_m = \sum_l S_{ml} b_l'$$

$$= \sum_n A_{mn} c_n = \sum_n \sum_r A_{mn} S_{nr} c_r'$$

For diagonalization : $b_h' = \lambda_h c_h'$.

$$\therefore S_{mh} \lambda_h = \sum_n A_{mn} S_{nh}$$

Same as before – but infinite no of eqns for each h,

solved if $|A_{mn} - \lambda_h \delta_{mn}| = 0$.

Soluble if A_{mn} has certain properties. .

λ_h's are called eigenvalues of A.

and ψ_h' is h^{th} eigenfunction of A.

and $A\psi_h' = \lambda_h \psi_h'$

For $A\psi = \sum_i b_i' \psi_i'$

$= \sum \lambda_i c_i' \psi_i'$ } equate coefficients

$= \sum c_i' A\psi_i'$

In elementary Q.M., energy operator usually considered;

In primed representation, A is diagonal : $A_{ih}' = \int \psi_i'^* A \psi_h'$

$= \lambda_h \int \psi_i'^* \psi_h' = \lambda_h \delta_{ih}$.

If a diagonal matrix is Hermitian,

must be real, for must have $A_{ih}' = A_{hi}'^*$

or $\lambda_h = \lambda_h^*$, $\therefore \lambda_h$ real. .

Is A' Hermitian, if A was?

Now $S_{mh} \lambda_h = \sum_n A_{mn} S_{nh}$

or $SA' = AS$

whence $A' = S^{-1} A S$

$\therefore A_{ih}' = \sum S_{im}^{-1} \sum A_{mn} S_{nh}$ but $S_{im}^{-1} = S_{mi}^*$

$$\therefore \quad A'_{ik} = \sum_{m,n} A_{mn} S^*_{mi} S_{nk}$$

$$A'_{ki} = \sum_{mn} A_{mn} S^*_{mk} S_{ni} = \sum_{mn} A_{nm} S^*_{nk} S_{mi}$$

~~$\therefore A'^*_{ki} = \sum_{mn} A^*_{nm} S_{nk} S^*_{mi} = \sum_{mn} A_{mn}$~~

$$\therefore A_{ki} = \sum_{mn} A^*_{mn} S^*_{nk} S_{mi} = A'^*_{ik} \quad .$$

(since A is Hermitian)

$\therefore$ if (A is Hermitian and S unitary), A′ also is .

Oct. 19

$$\Psi = \sum_m c_m \psi_m = \sum_m c'_m \psi'_m$$

where $c_m = \sum_k S_{mk} c'_k$

Whence $\psi'_k = \sum S_{nk} \psi_n$

$$A\psi = \sum_n b_n \psi_n \quad , \quad b_n = \sum_m A_{nm} c_m$$

$$A\psi = \sum_k b'_k \psi'_k \quad , \quad b'_k = \lambda_k c_k$$

$$S_{mk} \lambda_k = \sum_n A_{mn} S_{nk}$$

S determined by ↗ then solve $\| A_{mn} - \lambda_k S_{mn} \| = 0$.

+ get eigenvalues λ_k .

Now $\left[\begin{array}{l} S^*_{mk} \lambda^*_k = \sum_n A^*_{mn} S^*_{nk} \\ S_{mi} \lambda_i = \sum_n A_{mn} S_{ni} \end{array} \right. \quad \begin{array}{|l|} S_{mi} \\ S^*_{mk} \end{array} \quad \begin{array}{l} \sum_m \\ \sum_m \end{array}$

Then $(\lambda^*_k - \lambda_i) \sum S^*_{mk} S_{mi} = \sum A^*_{mn} S^*_{nk} S_{mi} - \sum A_{mn} S_{ni} S^*_{mk}$

But A is ~~Hermitean~~ ; $A_{mn} = A_{nm}^*$.

therefore $(\lambda_i^* - \lambda_k) \sum_m S_{mi}^* S_{mk} = 0$

~~either~~ $\lambda_i^* = \lambda_k$

or $\sum_m S_{mi}^* S_{mk} = 0$.

~~hence~~

Hence $\int \psi_i'^* \psi_k = \int \sum S_{mi}^* \psi_m^* \sum S_{nk} \psi_n$

$= \sum_{mn} S_{mi}^* S_{nk} \int \psi_m^* \psi_n$ (ψ's are orthogonal)

$= \sum_m S_{mi}^* S_{mk} = 0$

Hence new ψs, ψ' are ~~orthogonal~~ .

If $\lambda_i^* = \lambda_k$, $\sum S_{mi} S_{mk} \neq 0$, hence for degenerate ~~states~~ ψ's not orthogonal – (But we can take linear comb'n's that are ~~orthogonal~~).

Suppose we have degenerate ~~states~~ :

$A \psi_{k_j}' = \lambda_k \psi_{k_j}'$

can take $\psi_k = \sum a_j \psi_{k_j}$ + make them orthogonal

---

Reality ~~of eigenvalues~~ : $\lambda_k \underbrace{\sum_m S_{mk} S_{mk}^*}_{\text{real}} = \underbrace{\sum_{mn} A_{mn} S_{nk} S_{mk}^*}_{\text{real}}$ $\therefore \lambda_k$ real.

∴ if two eigen values are not equal, eigen functions are orthogonal; if they are equal can be made orthogonal.

$$\int \psi_k'^* \psi_k' = \sum_m S_{mk}^* S_{mk} = 1 \quad \text{for normalization.}$$

but if $\sum_m S_{mi}^* S_{mk} = \delta_{ik}$, S is unitary;

i.e. $S^{-1} = \tilde{S}^*$.

But if S is unitary, S^{-1} is also unitary, it changes primed f's to unprimed f's.

$$\psi_n = \sum_k S_{kn}^{-1} \psi_k' \qquad \Big[\text{for if } \psi_n = \sum T_{nk} \psi_k',$$

$$\psi_n = \sum S_{nk} T_{jn} \psi_j'$$

$$\therefore \sum T_{jn} S_{nk} = \delta_{jk}$$

$$\therefore TS = 1$$

$$\text{or } T = S^{-1} \Big]$$

also $c_k = \sum_n S_{kn}^{-1} c_n$

$$= \sum_n \tilde{S}_{kn}^* c_n$$

$$= \sum_n S_{nk}^* c_n$$

In words, $S_{nk} = \int \psi_n^* \psi_k'$

$$S_{kn}^{-1} = \int \psi_k'^* \psi_n = S_{nk}^*$$

If B is hermitian in unprimed system:

$B_{ik} = \int \psi_i'^* B \psi_k'$ it also is in new system.

Dirac Notation:

Suppose B is diagonal in ψ system; A is diagonal in ψ' system.

Denote eigenstates by B_n — Denote eigenstates by A_k

call transformation function $(B_n|A_k) = S_{nk}$

classical quantities are observables - A, B etc.

also write $c_n = (B_n|)$

$$\left(\text{i.e. } \psi = \sum (B_n|)\psi_n\right.$$

$(B_n|)$ are representation of state ψ

$$\text{then} \quad (B_n|) = \sum_k (B_n|A_k)(A_k|$$

Can have matrices of other observables in either representation;

$$\text{i.e.} \quad (B_m|C|B_n) = \int \varphi_m C \psi_n = \int \psi_m^* C \psi_n$$

$$\text{also} \quad (B_m|C|B_n) = \sum (B_m|A_i)(A_i|C|A_j)(A_j|B_n)$$

$$\left[\text{For} \quad \psi_n = \sum_k (B_k|A_n)\psi_k'\right.$$

$$S^{-1}_{kn} = (A_k|B_n)$$

$$\psi_m^* = \sum_i (A_i|B_m)^* \psi_i'^*$$

$$\left.(A_k|B_n) = (B_n|A_k)^* \quad \right]$$

matrix elements of C, in terms of eigenf'ns of A: $(A_i|C|A_k)$.

Transformation function $(A_k|B_n)$.

(Transforms axes in Hilbert space)

Expansion coefficients of arb. state: $(A_k|)$ $\qquad \Psi = \sum (A_k|)\psi_{A_k}$

then $(A_k|) = \sum (A_k|B_n)(B_n|)$ rel. of exp. coeff. of arb.

$\Psi_{B_n} = \sum (A_k|B_n)\psi_{A_k}$ rel. of eigenf'ns.

$(B_n|A_k)\,A_k = \sum (B_n|A|B_m)(B_m|A_k)$ determination of transf. f.

$(A_k|B_n) = (B_n|A_k)^*$ (Unitary matrix).

and $(A_i|C|A_k) = \sum_{mn} (A_i|B_m)(B_m|C|B_n)(B_n|A_k)$.

Main purpose of transf. theory is to calculate matrix elements in a convenient system of wave f'ns.

Example: Spin-Orbit interaction $\sim \underline{S}\cdot\underline{L}$.

S_{xyz} L_{xyz} J_{xyz}, S^2, L^2, J^2.

A representation: (L_3, S_3) $L_3(\mu)\,S_3(\sigma)$. want to get $(L_3(\mu)S_3(\sigma)|L\cdot S|L_3(\mu')S_3($

B ": (J_3, J) $J_3 = L_3 + S_3$ This can be done.

$J^2 = L^2+S^2+2L\cdot S$ but easier to get:

$(J_3(m)\,J^2(j)\,|L\cdot S|\,J_3(m')\,J^2(j$

Now need $(A_k|B_n)$

which is here $(L_3(\mu)S_3(\sigma)\,|\,J_3(m)\,J^2 j(j+1)) = \delta_{m,\mu+\sigma}\,(L_3(\mu)S_3(m-\mu)|J_3(m)$

Hence for each m, Ψ_{Bjm} contains at most $2s+1$ functions $\psi_{A\mu\sigma}$

$\sigma = -s \dots\dots +s$

$\mu = m+s \dots\dots m-$

We need $(\mu\sigma|J^2|\mu'\sigma')$

Then $(\mu\sigma|mj)\, j(j+1) = \sum_{\mu'\sigma'} (\mu\sigma|J^2|\mu'\sigma')(\mu'\sigma'|mj)$

Now $[J_3, L\cdot S] = 0$

$[J^2, L\cdot S] = 0$

$\therefore$ $L\cdot S$ matrix element vanishes unless $m = m'$; $j = j'$;

$\therefore$ $(mj|L\cdot S|m'j') = \delta_{mm'}\delta_{jj'}\frac{1}{2}[j(j+1) - l(l+1) - s(s+1)]$.

(since $L\cdot S = \frac{1}{2}(J^2 - L^2 - S^2)$).

Then use transf. fn to get matrix in μ,σ system.

---

largest $m = l+s$; $\mu = l$, $\sigma = s$

$(\mu\sigma|mj)\, j(j+1) = (\mu\sigma|J^2|\mu\sigma)(\mu\sigma|mj)$

$\longrightarrow = l(l+1) + s(s+1) + 2ls$

$= (l+s)(l+s+1)$

next: $m = l+s-1$; $\begin{cases}\mu = l & \sigma = s-1\\ \mu = l-1 & \sigma = s\end{cases}$

Here $(l, s-1|J^2|l, s-1)$, same as above;

but $(l-1, s|J^2|l, s-1)$, only $L_xS_x + L_yS_y$ give contribution;

$(l-1, s\; 2(L_xS_x + L_yS_y)\; l, s-1) = 2\sqrt{ls}$

etc.

(In this case, nothing saved -

Oct 24

Invariance of Spur of matrix $\text{Spur} = \sum_k A_{kk}$.

Spur is ~~invariant~~ against Unitary Transformation.

$$A'_{kk} = \sum_{mn} S_{km} A_{mn} S^{-1}_{nk}$$

$$\text{Spur} = \sum_k A'_{kk} = \sum_{kmn} S_{km} A_{mn} S^{-1}_{nk}$$

$$= \sum_{mn} A_{mn} \sum_k S_{km} S^{-1}_{nk}$$

Principle of Spectroscopic ~~Stability~~

$$= \sum_{mn} A_{mn} \delta_{mn}$$

$$= \sum_m A_{mm}$$

Eg: Transformation $\overset{L\,S}{\mu\sigma} \to \overset{A_3\,J^2}{mj}$

$$(\mu, m-\mu | C | \mu' m-\mu')$$

$$(m, j | C | m, j').$$

Spur: $\sum_\mu (\mu, m-\mu | C | \mu, m-\mu) = \sum_j (m, j | C | m j)$.

e.g. $(\mu\sigma | L\cdot S | \mu\sigma) = \mu\sigma$

largest value: $m = l+s$, $\mu = l$, $\sigma = s$

$\mu\sigma = ls$.

and $ls = (j = l+s | L\cdot S | l+s)$

But $L\cdot S$ commutes w. L, J, S, J_3

$L\cdot S$ depends, for given l & s, on j, but not on m;

if $m = l+s-1$ $\left.\begin{matrix}\mu = l-1 & \sigma = s \\ \mu = l & \sigma = s-1\end{matrix}\right\}$ $(\;|L\cdot S|) = \begin{cases}(l-1)s \\ (s-1)l\end{cases}$

Sum $= 2sl - l - s$

them in j rep., ~~the~~ one two states, one with $j = l+s$, $m = l+s-1$,
& one other.

Then by "spur invariant", we have;

$$2ls - l - s = (j \cdot l+s | L \cdot S | l+s) + (j' | L \cdot S | j')$$
$$= ls + (j' | L \cdot S | j')$$

$j' = l+s-1$

$$\therefore (j' | L \cdot S | j') = ls - l - s .$$

Keep this racket up until all j matrix elements are found

Method of sums. $j = l+s, l+s-1 \ldots \ldots |l-s|$.

~~Electrostatic~~ interaction of electrons –

e.g. p^2 ^1S ^1D ^3P calculation of energies by method of sums;

~~Take positi~~ 2 representations: μ_1, μ_2 and $\mu_1 + \mu_2$, ~~μ~~ L

→ sph. harmonics. $P_1^{\mu_1}(1) P_1^{\mu_2}(2)$.

Calculate $\frac{e^2}{r_{12}}$ matrix elements in $\mu_1 \mu_2$ rep;

then ~~to~~ transform to $\mu_1 + \mu_2$, L rep. by taking largest value first:

$\mu = 2$, $\mu_1 = \mu_2 = 1$, $L = 2$ ^1D

then $\mu = 1$ $\mu_1 = 1$ $\mu_2 = 0$ or $\mu_1 = 0$ $\mu_2 = 1$ $L = 2$ $L = 1$ ^3P

Calculate $(|\frac{e^2}{r_{12}}|)$ for these ↑ (diagonal), add them, subtract value for $L = 2$, & get value for $L = 1$.

Slater. P.R. '29

then $\mu = 0$ $\mu_1 = 1$ $\mu_2 = -1$; $\mu_1 = 0$ $\mu_2 = 0$; $\mu_1 = -1$ $\mu_2 = 1$ ~~L=2~~ $L = 0$

In second case, $E = \frac{e^2}{r_{12}}$ matrix is of form: $\begin{pmatrix} a & b \\ b & a \end{pmatrix}$ $\begin{matrix} 10 \\ 01 \end{matrix}$

If diagonalized, eigenvalues are $a \pm b$,
eigenfn's are sum & diff of original fn's.

(in fact, sum for ^1D state
diff. for ^3P state).

Third case,
^3P : $(1,-1) - (-1,1)$
^1S : $(1,-1) + (-1,1) + (0,0)$
^1D : $(1,-1) + (-1,1) - 2(0,0)$

~~Intermediate~~ coupling.	LS	j-j coupling.
	individual l's make a resultant L; individual s's make a resultant S	individual j's add up.
	valid if electrostatic ~~interaction~~ >> spin-orbit.	spin-orbit >> electrostatic.
	light atoms; 1st + 2nd rows of periodic table	X-ray spectra + heavy elements spectra; satellites emitted when atom is ionized in two different places —

~~Intermediate~~ coupling prevails for outer shells of heavy elements. $Z > 30$. Neither approximation valid.

Spectroscopic ~~Stability~~ helps: Take all levels of given J; consider LS + $j_1 j_2$ representations; & consider section corresp. to given J; calculate elst. + sp.orb. elements in each system. But this is more than necessary, for if you sum diagonal elements get same result in both

system, then calculate simple one & get rest from Spur invariance

By getting diagonal elements only, in all reps, can calculate complete matrices –.

Oct. 29 ~~Method~~ of sums used to find matrix elements in new representation –

Three representation A, B, C; A, B, C, diagonal in each one respectively.

$(C_j|C|C_k) = \delta_{jk} C_k$ when C_k are eigenvalues.

$(A_l|C|A_m)$, $(B_n|C|B_p)$; can transform these to ⤴ by looking for roots of ~~determinant~~:

$$\|(A_l|C|A_m) - \delta_{lm}\lambda\| = 0$$

$$\|(B_n|C|B_p) - \delta_{pn}\lambda\| = 0$$

algebraic eq'n's of ~~N~~ N^{th} order for λ; must have same roots, hence same coefficients.

∴ can equate coefficients in two representations.

$$\begin{vmatrix} C_{11}-\lambda & C_{12} & C_{13} & \\ C_{21} & C_{22}-\lambda & C_{23} & \cdots \\ C_{31} & \cdots & \cdots & \ddots \\ \vdots & & & C_{NN}-\lambda \end{vmatrix} = (-1)^N \lambda^N + (-1)^{N-1}\lambda^{N-1}\sum_k C_{kk} + \cdots + \cdots + \|C_{ij}\| = 0$$

C

each coefficient invariant, hence spur same in A, B, C rep

Prove: invariance of ~~determinant~~ $\|A_{lm} - \delta_{lm}\lambda\|$ from unitary character of ~~transformation~~]

$$\therefore \sum_l (A_l|C|A_l) = \sum_k (B_k|C|B_k) = \sum_k C_k$$

Take matrix of M_x in M_z representation and prove the invariance of spur + determinant $\| (M_{zm} | M_x | M_{zm'}) \|$ for transf. to principal axes.

Repeated Transformations.

$$(A_k |) = \sum_m (A_k | B_m)(B_m |)$$

$$(A_k | C | A_l) = \sum_{m n} (A_k | B_m)(B_m | C | B_n)(B_n | A_l)$$

Sometimes want to transform from one to another rep. then a third; suppose I know $(D_p |)$ but not $(B_m |)$.

then $$(A_k |) = \sum_{m p} (A_k | B_m)(B_m | D_p)(D_p |)$$

then $$(A_k | D_p) = \sum_m (A_k | B_m)(B_m | D_p)$$

Continuous variables –

i.e. variables with continuous range of eigenvalues.

If B has continuous range of eigenvalues: replace sums by integrals;

$$(A_k |) = \int (A_k | B') \, dB' (B' |)$$

Normalization: $\sum_n (A_k | B_n)(B_n | A_l) = \delta_{kl}$

or here: $\int (A_k | B') \, dB' (B' | A_l) = \delta_{kl}$

But $(B' | A_l) = (A_l | B')^*$

$\therefore \int (A_k | B')(A_l | B')^* \, dB' = \delta_{kl}$

if A is energy, B coordinate x, $(A_k | B')$ [illegible]

eigenfunction of Energy, expand as f'ns of coordinate x.

∴ ~~Orthogonality~~ relation is a special case of the unitary character of transformation function. obtained by taking coordinate as one of observables).

Now $(A_k | B_m)$ is dimensionless if k, m have discrete values.

But $(A_k | B')$ has dimension $\frac{1}{\sqrt{B}}$ if B has continuous eigenvalues.

(Schrödinger f'ns : dim $\frac{1}{\sqrt{l}}$ or $\frac{1}{\sqrt{l^3}}$ in 3 dimensions.

Now $\sum_k (B_m | A_k)(A_k | B_n) = \delta_{mn}$

$\sum_k (B' | A_k)(A_k | B'') = ?$ something has dimension of $\frac{1}{B}$.

can't be δ_{mn} – no meaning; introduce δ-function

if $F(B', B'') = \sum_k (B' | A_k)(A_k | B'')$

expand F in eigen f'ns of A;

$$F(B', B'') = \sum \varphi_l \psi_{A_l}(B'')$$

then $\varphi_l = \int \psi^*_{A_l}(B'')\, dB''\, F(B', B'')$

but $\psi^*_{A_l} = (B'' | A_l)$

$$\therefore \varphi_l = \int_B \sum_k (B' | A_k)(A_k | B'')\, dB''\, (B'' | A_l)$$

$$= \sum_k (B' | A_k)\, \delta_{kl}$$

$$= (B' | A_l).$$

i.e. $F(B', B'')$ is such a f'n that it gives no wt. to values of B'' different from B';

Hence $F(B', B'') = 0$ if $B'' \neq B'$

[i.e. ~~integrate~~ sum f'n × F over a range of B'' not including B', get 0

but $\int_{B'-\epsilon}^{B'+\epsilon} F(B', B'')\,dB'' = 1$; (i.e. integrate sum f'n over interval including B', & get ~~the~~ value of f'n at $B'' = B'$.

this is called Dirac's δ-function:

$$\delta(B''-B') = 0, \quad B'' \neq B'$$

and $\int_{B'-\epsilon}^{B'+\epsilon} \delta(B''-B')\,dB'' = 1$

Oct 31

$$\sum (B'|A_k)(A_k|B'') = F(B', B'') = F_{B'}(B'')$$

We showed that for any l, $\int (B''|A_l)(F_{B'}(B'')\,dB'' = (B'|A_l)$

also for any ψ: $\int \psi(B'')\,F_{B'}(B'')\,dB'' = \psi(B')$

Whence F must be δ function : $F(B'', B')$ for $B' \neq B''$

$\int F\,dB'' = 1$

$\therefore F(B'' B') = \delta(B''-B')$

Can consider δ to be the limit of a function: (e.g. $\delta(x) = \lim_{\alpha \to 0} e^{-\frac{x^2}{\alpha^2}} \cdot \frac{1}{\alpha\sqrt{\pi}}$)

Can also define $\delta(x, y, z) = 0$ if $x \neq 0$ or $y \neq 0$ or $z \neq 0$

and $\int_{-\epsilon}^{\epsilon} \delta\,d\tau = 1$

or something, $\delta(\theta, \varphi) = 0$ if $\theta \neq 0$ or $\varphi \neq 0$

& $\int \delta\,d\omega = 1$

Suppose A is energy, B is coördinate.

then $(A_k | B'') = \psi_k(B'')$ eigenf'n of kth eigen value of energy.

then $\sum_k \psi_k^*(B') \psi_k(B'') = \delta(B''-B')$

If we sum over a finite no. of states:

$$\sum_{k=1}^{N} \psi_k^*(B') \psi_k(B') = \rho(B', B'')$$ – "mixed density"

If we take all states with ~~λ_0~~ $\lambda > \lambda_0$, then if B' is more than λ_0 away from B'', ρ is ~~f~~ very nearly 0. , hence $\rho \simeq \delta(B'$

In theory of metals – make use of mixed densities in calcul. of correlation energies

In atoms, wave-fn's "avoid" each other – $\sum \psi_i^*(B'') \psi_k(B') \sim 0$ for $B'' \neq$

In position theory: ~~must~~ sum over all states of neg. energy to find properties; to find physical effect, must subtract actual (infinite) density from that.

Look at calculation of correlation energy – Wigner & Seitz PR 1933 ...

Suppose A also continuous.

then $\int (B'|A')(A'|B'') dA' = \delta(B''-B')$

if B is energy, A the coordinates: continuous eigenf'n's; they are orthogonal; but $\int (B'|A') dA' (A'|B') = \int |\psi|^2$ not defined;

but $\int \psi^*_{E'}(x) \psi_{E''}(x) = \delta(E'-E'')$

$$\therefore \quad \int \psi^*_{E'}(x)\,dx \int_{\mathcal{E}} \psi_{E''}(x)\,dE'' = \begin{cases} 0 & \text{if } E' \notin \mathcal{E} \\ 1 & \text{if } E' \subset \mathcal{E} \end{cases}$$

We want this to be true:

$$\Psi = \sum_n (x|E_n)(E_n|) + \int (x|E')\,dE'\,(E'|)$$

$$(E_n|) = \int (E_n|x)\,dx\,\psi(x)$$

$$(E'|) = \int (E'|x)\,dx\,\psi(x)$$

If this is to be true, must have

For continuum: $(E'|) = \int (E'|x)\,dx \int (x|E'')\,dE''\,(E''|)$ whence we must have

which is ~~$\int \psi^*_{E'}\,dx \int \psi_{E''}$~~ $\int (E'|x)\,dx \int (x|E'')\,dE'' = \delta($

If a problem has $V \neq 0$ only in a finite region, ~~then~~ then asymptotically, as $x \to \infty$, E is kinetic: $\frac{p^2}{2m}$ so a momentum state corresponds to an energy ~~state~~. [e.g. at large distances from atom no V, only kinetic E, & each E has a wave number]

Can talk about E, p, or k – all equivalent. ($k = p/\hbar$)

Expand: $\psi = \int (x|E')\,dE'\,(E'|) = \int (x|p')\,dp'\,(p'|)$ or $\int (x|k')\,dk'($

in eigenf'ns at large distance from free field).

$(x|E')$ differs from $(x|p')$ only by constant factors.

$$(x|E') = \alpha\,(x|p')$$

$$\therefore \int (E'|x)\,dx \int (x|E'')\,dE'' = \begin{cases} 0 \\ 1 \end{cases} \qquad \therefore \alpha^2 \int (p'|x)\,dx \int (x|p'')\,dE'' = \begin{cases} 0 \\ 1 \end{cases}$$

$$\int (p'|x)\,dx \int (x|p'')\,dp'' = \begin{cases} 0 \\ 1 \end{cases} \qquad \therefore \alpha^2 = \frac{dp''}{dE''} \qquad \therefore (x|A') = (x|B')\sqrt{\frac{dB'}{dA'}}$$

Dimensions:

$$[(A_k|B_k)] = 1$$

$$[(A_k|B')] = \frac{1}{\sqrt{B}}$$

$$[(A'|B')] = \frac{1}{\sqrt{AB}}$$

Hence

$$[(x|A')] = \frac{1}{\sqrt{\ell A}}$$

$$[(x|B')] = \frac{1}{\sqrt{\ell B}}$$

$$\therefore [(x|A')] = [(x|B')]\left[\sqrt{\frac{B}{A}}\right].$$

same result.

Nov. 5 [F.D.R. | W.L.W. | N.T. | E.B. | R.B.] ELECTION!

$$\int (A'|x')\,dx'\,(x'|A'') = \delta(A''-A')$$

$$\int (A'|x')\,dx' \int_{\varepsilon} (x'|A'')\,dA'' = \begin{cases} 1 & A' \in \varepsilon \\ 0 & A' \notin \varepsilon \end{cases}$$

Hydrogen atom:

$$c_k \frac{\sin(kr-\delta)}{r}\, Y_{\ell m}(\theta,\phi).$$

$$\int |Y|^2\,d\omega = 1$$

$$c_k^2 \int r^2 dr\, \frac{\sin(kr-\delta)}{r} \int_{k-\varepsilon}^{k+\varepsilon} \frac{\sin(k'r-\delta)}{r}\,dk'$$

$$= c_k^2 \int_0^\infty \sin(kr-\delta)\,dr \int_{k-\varepsilon}^{k+\varepsilon} \sin(k'r-\delta)\,dk$$

$$= c_k^2 \int \sin(kr-\delta)\,dr \left[-\frac{\cos(k'r-\delta)}{r} \Big|_{k-\varepsilon}^{k+\varepsilon} \right]$$

$$= c_k^2 \int \sin(kr-\delta)\,dr \cdot 2\sin(kr-\delta)\frac{\sin\varepsilon r}{r}$$

$$= 2c_k^2 \int_0^\infty dr\, \sin^2(kr-\delta)\frac{\sin\varepsilon r}{r} = 1$$

in limit as $\varepsilon \to 0$, $k \gg \varepsilon$, and $\sin^2(kr-\delta)$ varies so rapidly in comparison with $\sin\varepsilon r$, that we can replace it by its average - $\frac{1}{2}$.

$$\therefore \quad c_k^2 \int_0^\infty \frac{\sin\varepsilon r}{r}\,dr = 1$$

$$\frac{\pi}{2} c_k^2 = 1$$

$$\therefore c_k = \sqrt{\frac{2}{\pi}}$$

Normalization for unit wave number.

Normalization for unit energy: $\sqrt{\frac{2}{\pi}}\sqrt{\frac{dk}{dE}}$ $\quad \frac{dE}{dk} = \hbar\frac{dE}{dp} = \hbar v$

Matrices representing variable canonically conjugate to diagonal matrix
e.g. how is momentum represented in x-representation?

$$(x'|p')\,p = p(x'|p')$$

$$= -i\hbar\frac{\partial}{\partial x'}(x'|p')$$

$$\therefore (x'|p') = C e^{\frac{i}{\hbar}p'x'}$$

$$= \frac{1}{\sqrt{2\pi}} e^{\frac{i p'x'}{\hbar}}$$

momentum "eigenf'ns": $\quad (p'|E') = \int (p'|x')dx'(x'|E') = \frac{1}{\sqrt{2\pi}}\int \psi(x') e^{-\frac{ip'x'}{\hbar}}dx'$

$|(p'|E')|^2$ gives prob of finding particle with mom. in dp', when it is in energy state E' —

We want to find: $(x'|p|x'') = \int (x'|p')\,dp'\,p'\,(p'|x'')$

$$= \int \frac{1}{2\pi}\, e^{\frac{ip'x'}{\hbar}}\, p'\, dp'\, e^{-\frac{ip'x''}{\hbar}}$$

$$= \frac{1}{2\pi}\int p'\, e^{\frac{i}{\hbar}p'(x'-x'')}\, dp'$$

$$= \frac{1}{2\pi}\,\frac{\hbar}{i}\,\frac{\partial}{\partial x'}\int e^{\frac{i}{\hbar}p'(x'-x'')}\, dp'$$

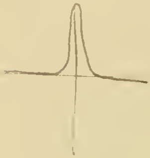
$$= -\frac{i\hbar}{2\pi\hbar}\,\frac{\partial}{\partial x'}\int (x'|p')\,dp'\,(p'|x'')$$

$$= -i\hbar\,\frac{\partial}{\partial x'}\,\delta(x'-x'') \qquad !$$

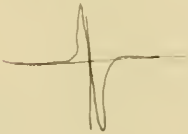
$$= -i\hbar\,\delta'(x'-x'')$$

Matrix of p is given by derivative of δ fn !

$\delta(x)$:



$\delta'(x)$:



$\delta'(x) = 0$ for $x \neq 0$.

and $\int_{-\epsilon}^{\epsilon}\delta'(x)\,dx = \delta(\epsilon) - \delta(-\epsilon) = 0$.

but $\int_{-\epsilon}^{\epsilon} dy \int_{-\epsilon}^{y}\delta'(x)\,dx = 1$

but $\longrightarrow = \int_{-\epsilon}^{\epsilon}\delta'(x)\,dx\int_{x}^{\epsilon} dy$

$$= \int_{-\epsilon}^{\epsilon}\delta'(x)(\epsilon - x)\,dx$$

$$= -\int_{-\epsilon}^{\epsilon} x\,\delta'(x)\,dx = 1 \qquad !$$

Now $\int f(x)\,\delta(x-x')\,dx = f(x')$.

$$\int f(x)\,\delta'(x-x')\,dx = \delta(x-x')\,f(x)\Big| - \int \delta(x-x')\,f'(x)\,dx$$

$$= -f'(x').$$

Applying to momentum matrix!

$$(x'|p|x'')f(x'') = -i\hbar\,\delta'(x'-x'')f(x'') = 0 \text{ unless } x' = x''$$

$$\int(x'|p|x'')dx''f(x'') = -i\hbar f'(x')$$

Nov. 7

In 3 dimensions, ~~[illegible]~~ need ~~[illegible]~~ 3 coordinates x_1, x_2, x_3; use $x_{1,2,3}$ representation — they all commute.

In general, if no symmetry, the ~~[illegible]~~ discrete energy levels give a complete description of state.

If there is symmetry — e.g. spherical — state describable by E & M_3. (degeneracy; for different M_3, same E).

Coulomb field: more degeneracy, E, M_3, M^2; (or different quantities in parabolic coordinates).

If E has continuous eigenvalues —

If spherical symmetry, separable in polar coord's — again E, M^2, M_3 can be quantized;

If E continuous, no sph. symm., E doesn't commute w. M^2, M_3, must choose 3 other commuting observables — can use E, Θ, Φ — direction of motion at large distance from center of force

---

Some transformations have very simple physical meaning; e.g. transf. from coordinates to momentum simply is a Fourier analysis.

Apply p_x to a function $\psi(x)$.

$$p_x \psi(x) = -i\hbar \frac{\partial}{\partial x} \psi(x)$$

Momentum operator is connected with translation in space.
Angular mom. " . . . . . . rotation " " .

$$M_3 \psi = -i\hbar \frac{\partial}{\partial \varphi} \psi$$

If several particles: $M_{3,1} \psi = -i\hbar \frac{\partial}{\partial \varphi_1} \psi$ — rotation of individual (electron)

and total orbital $M_3 = \sum_k M_{3k} \psi = -i\hbar \sum_k \frac{\partial \psi}{\partial \varphi_k}$ —

M_3 corresponds to rotation of whole system (potential energy not changed). (hence $[E, M_3] = 0$.)

[In general, an operator associated with a change of a mechanical system in which potential energy remains unchanged, commutes with energy.]

Total, orbital + spin corresponds to rotation of spin as well as space coord. about z axis —

---

p will commute w. E if a translation doesn't change potential (i.e. field-free particle).

Total momentum commutes w. E if only interaction between particles

(i.e. centre of mass moves as free particle)

Finally $E = i\hbar \frac{\partial}{\partial t}$.

Energy corresponds to time rate of change of ψ.

Sum of ~~states~~ – $\sum_n e^{-\frac{E_n}{kT}}$ (including integral over continuum)

according to invariance of sum of diagonal elements,

~~Th~~ $\sum_n e^{-E_n/kT}$ is the same for any representation since it is sum of diagonal elements of $e^{-H/kT}$

$$\therefore \sum_n e^{-\frac{E_n}{kT}} = \text{Spur}\left(x' \middle| e^{-\frac{H}{kT}} \middle| x''\right).$$

$$= \int dx' \left(x' \middle| e^{-H/kT} \middle| x'\right)$$

$$= \int dx' \sum_n \left(x' | E_n\right)\left(E_n \middle| e^{-H/kT} \middle| E_n\right)\left(E_n | x'\right)$$

$$= \int dx' \sum_n \left(x' | E_n\right) e^{-E_n/kT} \left(E_n | x'\right)$$

$$= \int dx' \sum_n \psi_n^*(x') e^{-\frac{E_n}{kT}} \psi_n(x')$$

if we replace kT by $-\frac{i\hbar}{t}$, we have:

$$= \int dx' \sum_n ~~\#~~ u_n^*(x', 0), u_n\left(x', -\frac{i\hbar}{kT}\right)$$

Where $u_n(x', t) = \psi_n(x') e^{-\frac{iE_n t}{\hbar}}$

$$= \int \rho\left(x', 0; x', -\frac{i\hbar}{kT}\right) dx'$$

Bloch Ferromagnetism

defining mixed density $\rho(x't'; x''t'') = \sum u_n^*(x't') u_n(x''t'')$

Group Theory

In physics only a small part of group theory is used —

Group of eraser: those ~~rotat~~ transformations which give the same thing again - ~~i.e.~~ e.g. rotation about 3 axes thru 180°:

E A B C

E - identity
A - rotation about x
B - " " y
C - " " z

$A^2 = B^2 = C^2 = E$;

$EA = A$
$EB = B$
$EC = C$
$AB = C = BA$ (in this case only)
$AC = B = CA$
$BC = A = CB$.

Multiplication table:

	E	A	B	C
E	E	A	B	C
A	A	E	C	B
B	B	C	E	A
C	C	B	A	E

Can have groups with finite or infinite no. of elements

i, -i, -1
(not quite)

Nov. 9 | Any element A times other elements x gives whole group.

The above group is Abelian - i.e. AB = BA etc ~~commutation~~.

The elements of a group might be represented by a number of things; e.g. transformations in space; permutations, matrices, ordinary numbers, etc. —

Simplest group:

	E	A
E	E	A
A	A	E

might represent rotation of line about 180°
or permutation of two numbers (1 2);

$E \sim (1,2)$
$A \sim (2,1)$

or numbers $1, -1$;

$E = 1,\ A = -1$; $(1)(1) = 1$, $(-1)(-1) = 1$, $(-1)(1) = -1$, $(1)(-1) = -1$;

These are representations of the (abstract) group; by numbers or rotations obeying same multiplication table

With two elements E, A, only one possibility: $A^2 = E$;

With three elements E, A, B:

$AE = A$,

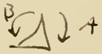
if $AA = E$, must have $AB = B$ which is impossible

hence must have $AA = B$, $AB = E$:

Then $B = A^{-1}$, inverse.

	E	A	B
E	E	A	B
A	A	B	E
B	B	E	A

each element of a group must have an inverse in the group;
i.e. that x for which $Ax = E$ is inverse of A.

rotation of equilateral triangle: 

$B = A^{-1}$;
also $B = A^2$;
$B^3 = A^3 = E$

or: $\sqrt[3]{1} = \begin{cases} 1 \\ -\frac{1}{2} + \frac{1}{2}\sqrt{3} \\ -\frac{1}{2} - \frac{1}{2}\sqrt{3} \end{cases}$.

three possible:

A	B	E
(1)	(1)	(1)
$(-\frac{1}{2} + \frac{1}{2}\sqrt{3})$	$(-\frac{1}{2} - \frac{1}{2}\sqrt{3})$	(1)

one trivial.

Now suppose we have a potential V such that V(r) is unchanged if V(r) is rotated thru 120° around the z-axis — Then $\psi(r)$ ~~A~~, $\psi(Ar)$ satisfy the same Schrödinger equation (A represents the rotation). If eigenvalue is non-degenerate,

$$\text{whence} \quad \psi(Ar) = c_A \psi(r)$$

$$\text{also} \quad \psi(Br) = c_A^2 \psi(r)$$

$$\psi(AB)r) = \psi(r) = c_A^3 \psi(r)$$

$$\therefore c_A^3 = 1$$

$$\text{and } c_A = \sqrt[3]{1}$$

∴ the coefficient c_A is a representation of the group (A, B, E)

This illustrates one of chief uses of group theory — i.e. to investigate wave-fns under transformations which leave V unchanged; e.g. rotations, in sph. sym. field; or permutations, if many electrons; etc. It turns out that ~~most of~~ treatment of rotations + permutations can be done without group theory — but it helps give more insight.

Restricted rotation group (finite no of rotations) very useful in theory of electrons in crystal lattices.

Permutation group in nuclear physics (uses different representations than in atomic physics — since two spin states for a given space in atomic, 4 in nuclear).

Coming back to 120° rotation:

Consider a fn $\psi \sim e^{im\varphi}$. How does it transform under operations A, B, E?

$$A: \ \varphi \to \varphi - 2\pi/3$$

$$\psi \to e^{-im\,2\pi/3}\psi = (-\tfrac{1}{2} - \tfrac{i}{2}\sqrt{3})^m \psi .$$

For a single-valued fn, m = integer, and coeff is one of $\sqrt[3]{1}$

for m = 1, 4, 7 --- get 1st representation;
m = 2, 5, 8 - - " 2nd "
m = 3, 0, 9 - - " 3rd " (1, 1, 1).

If we have a fourier-expandable function:

$$\psi \sim \sum_n a_n e^{in\varphi}$$

there occur in the series: $m = 3n$ n integer
or $= 3n+1$
or $= 3n-1$

Suppose we add to $V(r)$ a small $U(r)\cos 3\varphi$;

$$\Psi \sim \psi(r)\, Y_{lm}(\theta\varphi)$$

$$\sim \psi_r\, P_{lm}(\theta)\, e^{im\varphi} \quad \text{E doesn't depend on } m$$

Now consider perturbation $U(r)\cos 3\varphi$;

Must consider matrix elements between degenerate states; i.e. splitting of levels by perturbation; i.e.:

$$U(r)\,|\psi(r)|^2\, P_{lm}(\theta) P_{lm'}(\theta)\, e^{i(m-m')\varphi} \cos 3\varphi \; dr\, d\Omega$$

(integral $\neq 0$ only if $m - m' = \pm 3$.

Hence there are 3 sets of eigenfn's with same l; and elements only between states of same set

Hence matrix is: (e.g. for $l=2$)

m:	2	1	0	-1	-2
2	0	0	0	α	0
1	0	0	0	0	β
0	0	0	0	0	β_0
-1	α^*	0	0	0	0
-2	0	β^*	0	0	0

And ~~zero-order~~ first approx eigenf'ns contain either $m = 2, -1$; } general or $1, -2$; } f'ns; or 0 but not other mixtures.

Same result as before – i.e. group theory told us with little work some of properties of eigenfn's under this perturbation.

Suppose now we have an optical transition polarized in z-direction – must calculate: $\int \psi_f^* \, z \, \psi_i$ z is operator unchanged by A or B.

Hence ~~z~~ integral should remain unchanged under rotation

$$\therefore \quad \psi_i(A\lambda)\,\psi_f^*(A\lambda) = \psi_i(\lambda)\,\psi_f^*(\lambda);$$

$$\text{i.e.} \quad c_{A_i} c_{A_f}^* = 1$$

$$\therefore \quad c_{A_f} = c_{A_i} \quad \text{– i.e.}$$

Optical transitions only between states of same representation

---

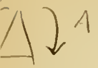
Nov. 12 Rotations of equilateral triangle.

E, A, B, ; $B = A^2$ $AB = E = A^3 = B^3$.
$A = B^2$.

$$\psi(A\lambda) = c_A \psi(\lambda) \qquad c_A = \sqrt[3]{1} = \begin{cases} 1 \\ e^{\frac{2}{3}i\pi} \\ e^{-\frac{2}{3}i\pi} \end{cases}$$

$$\psi(B\lambda) = c_B \psi(\lambda)$$

Consider properties of $\cos m\varphi$, $\sin m\varphi$ under this transformation.



$$A: \cos m\varphi \to \cos m(\varphi - \tfrac{2}{3}\pi)$$

$$\psi_1 = \cos m\varphi \qquad = \cos\tfrac{2m\pi}{3}\cos m\varphi + \sin\tfrac{2m\pi}{3}\sin m\varphi$$

$$\psi_2 = \sin m\varphi \qquad A: \sin m\varphi \to \sin m(\varphi - \tfrac{2}{3}\pi)$$

$$\cos\tfrac{2m\pi}{3}\sin m\varphi - \sin\tfrac{2m\pi}{3}\cos m\varphi .$$

$$\psi(A1) = a_{11}\psi_1(1) + a_{12}\psi_2(1)$$

$$(e) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (b) = \begin{pmatrix} \cos\frac{m\pi}{3} & -\sin\frac{m\pi}{3} \\ \sin\frac{m\pi}{3} & \cos\frac{m\pi}{3} \end{pmatrix} \quad (a) = \begin{pmatrix} \cos\frac{2}{3}m\pi & \sin\frac{2}{3}m\pi \\ -\sin\frac{2}{3}m\pi & \cos\frac{2}{3}m\pi \end{pmatrix}$$

If $m = 3n$, $\psi_1(A1) = \psi_1(1)$

$m = 3n \pm 1$

Two-dimensional representation - repr. by matrices of 2 rows & columns.

$$A = \begin{pmatrix} \cos & \sin \\ -\sin & \cos \end{pmatrix}$$

$$B = A^2 = \begin{pmatrix} \cos & \sin \\ -\sin & \cos \end{pmatrix}^2 = \begin{pmatrix} \cos & -\sin \\ \sin & \cos \end{pmatrix}$$

$$AB = \begin{pmatrix} \cos & \sin \\ -\sin & \cos \end{pmatrix}\begin{pmatrix} \cos & -\sin \\ \sin & \cos \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = E .$$

If we go from these ψ's back to $\psi = e^{im\varphi}$.

$$\psi_i' = \sum_k S_{ik}\psi_k$$

$$\psi_k(A1) = \sum A_{kl}\psi_l(1)$$

$$\psi_i'(A1) = \sum_k\sum_l\sum_m S_{ik}A_{kl}S^{-1}_{lm}\psi_m'(1)$$

$$A' = S A S^{-1} \qquad \text{(unitary transf. of representation)}$$

In this case, transf. S takes group matrices to principal axes simultaneously: ~~—~~ and get 2 one-dimensional

$S_1' = \ldots$

~~$S = \ldots$~~ $\quad S_2' = \ldots$ representations. We say the

~~$S^{-1} = \frac{1}{2}(\ldots)$~~ 2-dim. rep. is reducible to

~~$\frac{1}{\sqrt{2}}(\ldots)(\ldots) = \frac{1}{2}(\ldots)(\ldots) = \frac{1}{2}(\ldots)$~~

2 - one dimensional representations.

In general, an n-dimensional rep. of a group will sometimes be <u>reducible</u>, [to, e.g. 2 $\frac{n}{2}$-dimensional rep.'s] by a unitary transformation. [i.e. SXS^{-1} becomes several matrices of less than n-dim. simultaneously for all X].

If no such S, representation is irreducible.

Irreducible transf. of certain groups ~~important~~.

3-dim. rotations:

Wave fns $\quad l = 1 \qquad \left.\begin{matrix} \cos\theta \\ \sin\theta\, e^{i\varphi} \\ \sin\theta\, e^{-i\varphi} \end{matrix}\right\} \sim \left\{\begin{matrix} z/r \\ x/r \\ y/r \end{matrix}\right.$

These are transformed into linear combinations of each other by rotations; none of them is always transformed into ~~itself~~ -

But if we have six f'ns: $\quad \cos^2\theta \qquad \sin\theta\cos\theta\, e^{i\varphi}$

$\sin^2\theta\, e^{2i\varphi} \qquad \sin\theta\cos\theta\, e^{-i\varphi}$

$\sin^2\theta\, e^{-2i\varphi} \qquad \sin^2\theta$

which is invariant under rotation ; Hence 6 dim. ~~group~~
can be broken up into one 5 + one 1 - dimensional ~~group~~ representation

---

Group of 4 elements.

Two distinct ones.

	E	A	B	C
E	E	A	B	C
A	A	E	C	B
B	B	C	E	A
C	C	B	A	E

or

	E	A	B	C
E	E	A	B	C
A	A	E	C	B
B	B	C	A	E
C	C	B	E	A

$\longrightarrow$ $A^2 = E$, $B^2 = A$, $B^3 = AB = C$, $B^4 = A^2 = E$, $C^2 = B^6 = A$, $C^3 = B^9 = C$, $C^4 = B^{12} = E$, $A^2 = E$, $A^3 = A$, $A^4 = E$

I

$A^2 = E$
$B^2 = E$
$C^2 = E$
$AB = C$
$BC = A$
$CA = B$;

All elements the same.

rotations of parallelopipd (e.g. eraser)

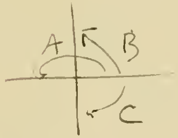
II B & C the same.

3 kinds of elements :

E, A, B & C.

group of rotations of square in plane.

II - by giving representation of B (or C) can get all of them.



$BC = E$
$B^2 = C^2 = A$
etc.

$B^4 = E$ $c_B^{\,4} = 1$

$\therefore c_B = 1, i, -1, -i$.

$e^{i m \pi/2}$, $m = 4n,\ 4n+1,\ 4n+2,\ 4n+3$

$C_A = c_B^2 = 1, -1, 1, -1$

$C_C = 1, -i, -1, i$

$C_E = 1, 1, 1, 1$.

4 representations.

in case I : $C_A^2 = 1$ $C_B^2 = 1$ $C_C^2 = 1$

$C_A = \pm 1$ $C_B = \pm 1$ $C_C = \pm 1$

4 representations :

	1	2	3	4
E	1	1	1	1
A	1	1	-1	-1
B	1	-1	1	-1
C	1	-1	-1	1

Nov. ~~13~~ 14.

Group all of whose elements can be got from taking powers of one of the elements is a cyclic group. ; and any such group can be represented by roots of unity.

If we have a cyclical group $O(h)$, $A^h = E$;

then $C_A = \sqrt[h]{1} = e^{\frac{2\pi i}{h} k}$

$k = 0, 1 \cdots h$

True representation : each element represented by a different matrix or number
Untrue " : several " " " the same " " " .

for $k = 1$, always get a True rep.
for $k = 0$, " " an untrue rep; namely, unit.

Four group : $A^2 = B^2 = C^2 = E$;

$AB = C$
$BC = A$
$CA = B$

we gave 4 untrue rep. of the group.

For a true rep.; if you know one, you know all the rest.

Five elements; only the cyclic group. (as always for primes).

Wigner - VII - IX

Six elements:

group of permutations of three quantities

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
F	F	B	C	A	E	D

Not Abelian.

permute	123 :	213	132	321	312	231
	E	A	B	C	D	F

$A^2 = B^2 = C^2 = E$; but $D^2 = F$, $F^2 = D$

$AB = D$ $AC = F$ $BC = D$
$BA = F$ $CA = D$ $CB = F$

$DF = FD = E$.

It has subgroups; (EA) (EB) (EC) (EDF) are all groups by themselves.

E	A
A	E

E	B
B	E

E	C
C	E

E	D	F
D	F	E
F	E	D

Co-sets: take elements of sub-group $\mathfrak{G}$ + multiply by an element not in the subgroup. If subgroup $\mathfrak{G}$ contains g elements, each coset contains g elements;

e.g.: a coset of (AE) is B, AB
$\mathfrak{E}B$ = B D. in this case.

the another is $\mathfrak{E}C$: (C, AC), = (C, F).

n^{th} coset given by $\mathfrak{S} X_n$ if X_n is any element of nth coset.

cosets not groups.

Subgroups $\underline{G_1}$ $\underline{G_2}$ $\underline{G_3}$ . . .

$$\underline{G} X_n = \underline{G_n} \text{ cosets} \qquad \underline{G}\,\underline{G_n} = g\,G_n$$

$$\underline{G}\, X_n X_m = \underline{G_n}\,\underline{G_m}$$

Two cosets identical in one element are identical in all elements.

The cosets form a group, with the original subgroup the unit element + cosets the other elements. $gn = h$

n = no. of cosets inclu. subgroup

g - order of subgroup

h - " " original group

Hence order of subgroup must be a divisor of order of group

if h is prime: no non-trivial subgroups.

In above case, $h = 6$, can have subgroups with $g = 2, 3$.

Classes. take any group elements X, A + find $X^{-1}AX$;

for any Abelian group $X^{-1}AX = A$.

not otherwise!

e.g. in above group, all elements got from $X^{-1}AX$, X all elements of group, form a class.

$C^{-1}AC = CF = B$

$B^{-1}AB = BD = C$

$D^{-1}AD = EB = C$

$F^{-1}AF = DC = B$

$A^{-1}AA = \quad = A$

$E^{-1}AE = \quad A$

$A^{-1}DA = AC = F$

Here E, A, B, C, D, F, form classes.

any element belongs to one & only one class.

If order of group is prime, it is cyclic, hence Abelian, and each element forms its own class.

In above group, E : no permutation.
A, B, C : ~~two~~ one ~~permutation~~ interchange
D, F : two ~~permutations~~. interchanges.

Cubic group: x, y, z can be interchanged.
hence 6 permutations.
sign of any coord can be interchanged
8 possibilities;
$\therefore 6 \cdot 8 = 48$ elements !.

Classes: $C_1 = E$ 1
C_2 : rotations about one of cubic axes thru $180°$ 3
C_3 : " " " " " " $90°$ 6
C_4 : " " body diagonal thru $120°$ 8
C_5 " " face " " " $180°$ 6
24

these 24 form subgroup of pure rotation.

For each of these classes there is another class, for which one takes mirror images:

I : inversion
IC_2 : " images at cubic planes
I_{-3} — — —

etc.

Nov. 16

E belongs to every subgroup:

E " " one & only one class, namely, class consisting of E a

In general, an element belongs to many subgroups, but only one class.

~~Multiplication~~ of classes:

Conjugate classes C_i & C_k

$X_i^{-1} A_i X_i = A_i'$ $X_k^{-1} A_k X_k = A_k'$

multiply $C_i C_k$:

in general, $C_i C_k$ contains elements of other classes; if it contains one, it contains all; If a product can be obtained in more than one way, all other products can be obtained in the same no. of ways. i.e. product contains all elements of any class the same no. of times.

e.g. in 6-group:

$(C_3)^2 = C_3 + 2C_1$

$(C_1)^2 = C_1$

$(C_2 C_3) = 2C_2$

$(C_2)^2 = 3C_1 + 3C_3$

$C_1 C_2 = C_2$

$C_1 C_3 = C_3$

Mult. table of classes in ↗:

C_1	C_2	C_3
C_2	$3(C_1 + C_3)$	$2C_2$
C_3	$2C_2$	$C_3 + 2C_1$

Representation: reducible if a transf. can simultaneously transform all matrices of group to $\left(\begin{array}{c|c} & 0 \\ \hline 0 & \end{array}\right)$ form.

If none such can be found, irreducible representation.

Operators correspond to ~~transformation~~ of wave opr's.

$\psi_i(\underline{A}\,x) = \sum_k A_{ik}\,\psi_k(x)$; A_{ik} is matrix representing

operation A of group.

Any representation can be ~~transformed~~ to a unitary one transformed . .

$$S^{-1} A_k S = \text{unitary matrix}$$

Consider $\sum_\kappa A_\kappa A_\kappa^\dagger = H$. $\qquad \dagger = \sim *$.

then H is Hermitian $\Big[$ for $H_{ih} = \sum_\kappa \sum_j A_{ij} A^\dagger_{jh}$

$= \sum_\kappa \sum_j A_{ij} A^*_{hj}$

$\mathcal{U}^{-1} H\, \mathcal{U} = d$ — diagonal matrix.

$H_{hi} = \sum_\kappa \sum_j A_{hj} A^\dagger_{ji}$

$= \sum_\kappa \sum_j A_{hj} A^*_{ij}$

Then $d^{-1/2}\,\mathcal{U}^{-1} H\, \mathcal{U}\, d^{1/2} = 1$ $\qquad = H^*_{ih}$.

Can show ~~that~~ $d^{-1/2}\,\mathcal{U}^{-1} A_\kappa\, \mathcal{U}\, d^{1/2}$ are unitary for all κ

See Wigner, pp 81-82.

If $A_\kappa M = M A_\kappa$ for all κ , $M_{ih} \neq \mathcal{U}_h\, \delta_{ih}$,

then the representation is reducible.

(& only then)

If $A_\kappa M = M A_\kappa$

then $M^\dagger A_\kappa^\dagger = A_\kappa^\dagger M^\dagger$

and $A_\kappa M^\dagger A_\kappa^\dagger A_\kappa = A_\kappa A_\kappa^\dagger M^\dagger A_\kappa$

$\therefore A_\kappa M^\dagger = M^\dagger A_\kappa$ (if A_κ are unitary, as they can be, by above theorem

$\therefore A_\kappa$ also commute w. $M + M^\dagger$ + $i(M - M^\dagger)$.

$M + M^\dagger$ are Hermitian

& $i(M - M^\dagger)$

Hence there exists a Hermitian matrix which commutes with all group elements.

Then can find an S such that:

$$S^{-1}MS \text{ is diagonal;}$$

$$\text{then } S^{-1}A_k S \cdot S^{-1}MS = S^{-1}MS \; S^{-1}A_k S .$$

But $S^{-1}A_k S = \bar{A}_k$ is a new unitary representation.

and $S^{-1}MS = d$, diagonal;

and $\bar{A}_k d = d \bar{A}_k$.

Now suppose $d_{ii} \neq d_{hh}$;

$$\text{then } \bar{A}^k_{ih} d_{hh} = d_{ii} \bar{A}^k_{ih} ;$$

$$\therefore \bar{A}_{ih} = 0 ;$$

Then if we order d like this: $\left(\begin{array}{c|c|c} d_1 d_1 & & \\ \hline & d_2 d_2 & \\ \hline & & d_3 \ldots \end{array} \right.$

And $A_{ih} = 0$ outside of diagonal squares;

whence it is reducible. $\left(\begin{array}{c|c|c} 2 & 0 & 0 \\ \hline 0 & 2 & 0 \\ \hline 0 & 0 & 2 \end{array} \right)$

(if d contains different elements).

[if d ~~not~~ is multiple unit matrix, $M = S^{-1} d S^{-1}$, also a multiple of unit matrix, contrary to assumption)

Nov 19

1. Group representations are unitary.
2. If M commutes with all the group matrices, the group representation is reducible, or else M is a multiple of 1.
3. Schur's Lemma.

If we have 2 representations $D^{(1)}(A_\kappa)$, $D^{(2)}(A_\kappa)$.
dim. l_1 l_2

suppose $\exists$ a matrix M s.t.:

(M has l_1 colums, l_2 rows.)

$$M D^{(1)}(A_\kappa) = D^{(2)}(A_\kappa) M \quad \text{for all } \kappa.$$

Then either $M \equiv 0$, $\leftarrow l_1 \neq l_2$
or $|M| = 0 \leftarrow l_1 = l_2$.

If $|M| \neq 0$, then M^{-1} can be found;
then $D^{(1)} = M^{-1} D^{(2)} M$, and
$D^{(1)}$ & $D^{(2)}$ are equivalent.

i.e. If $D^{(1)}$ & $D^{(2)}$ are non-equivalent irreducible representations, then $M = 0$)

$$M D^{(1)} = D^{(2)} M.$$

$$\therefore D^{(1)\dagger} M^\dagger = M^\dagger D^{(2)\dagger}$$

If group matrices are unitary, $D^{(1)\dagger}(A_\kappa) = D^{(1)}(A_\kappa^{-1}) = D^{(1)}[A_\kappa^{-1}]$
$D^{(2)\dagger} = D^{(2)-1}(A_\kappa) = D^{(2)}[A_\kappa^{-1}]$.

$$\therefore D^{(1)}[A_\kappa^{-1}] M^\dagger = M^\dagger D^{(2)}[A_\kappa^{-1}].$$

$$\therefore D^{(1)}[A_\kappa] M^\dagger = M^\dagger D^{(2)}[A_\kappa]$$

then $M D^{(1)} M^\dagger = M M^\dagger D^2$

$$M D^{(1)} M^{\dagger} = M M^{\dagger} D^{(2)}$$

but $M D^{(1)} = D^{(2)} M$;

$$\therefore D^{(2)} M M^{\dagger} = M M^{\dagger} D^{(2)}$$

$\therefore (M M^{\dagger})$ commutes with D^{2};

but since $D^{(2)}$ is irreducible, by previous theorem,

$$M M^{\dagger} = c\, I$$

Case $l_1 = l_2$: If $c \neq 0$, then $\| M M^{\dagger} \| = c^{l_1} \neq 0$.

$$\|M\| \|M^{\dagger}\| \neq 0.$$

~~thus~~ $\|M\| \neq 0$, and D^1 + D^2 equivalent

If $c = 0$, $\quad M M^{\dagger} = 0$,

$$\sum_i M_{ki} M_{ik}^{\dagger} = \sum_i M_{ki} M_{ki}^{*}$$

$$= \sum_i |M_{ki}|^2 = 0$$

(all positive)

$\therefore M_{ki} = 0$

$\therefore M = 0$.

Case $l_1 \neq l_2$:

amplify M: $\begin{pmatrix} M_{11} \cdots M_{1 l_1} \; 0 \cdots 0 \\ \vdots \\ M_{l_2 l_1} \; 0 \cdots 0 \end{pmatrix} = N$ ($l_2 - l_1$ zeros).

$$(M M^{\dagger})_{ij} = \sum_k M_{ik} M_{kj}^{\dagger}$$

$$= \sum_{k=1}^{l_1} M_{ik} M_{jk}^{*}$$

$(N N^{\dagger})_{ij} = (M M^{\dagger})_{ij}$ (extra terms are all zero)

then $\|MM^\dagger\| = \|VV^\dagger\| = \|V\| \, \|V^\dagger\| - \|V\|^2 = 0$

since V has lots of zeros.

$\therefore \; M \equiv 0$ as before.

If we construct an M which has the property of the theorem, it must be zero:

$$M = \sum_R D^{(2)}(R) \, X \, D^{(1)}(R^{-1}).$$

X is an arbitrary matrix of same dim. as M.

$$D^{(2)}(S) M = \sum_R D^{(2)}(S) D^{(2)}(R) X D^{(1)}(R^{-1})$$

$$= \sum D^{(2)}(SR) \, X \, D^{(1)}(R^{-1}).$$

if $R' = SR$ — R' goes thru all group elements if R does;

$R = S^{-1}R'$

$R^{-1} = R'^{-1}S$

$$\therefore \; D^{(2)}S \, M = \sum_{R'} D^{(2)}(R') \, X \, D^{(1)}(R'^{-1}S)$$

$$= \sum D^{(2)}(R') \, X \, D^{(1)}(R'^{-1}) \, D^{(1)}S$$

$$= M \; D^{(1)}(S).$$

Hence we must have:

(if $D^{(1)}, D^{(2)}$ not equivalent, + both irreducible)

$$\sum_R D^{(2)}(R) \, X \, D^{(1)}(R^{-1}) = 0.$$

Take $X_{hm} = 1$, $X_{h'm'} = 0$ if $h' \neq h$ or $m' \neq m$

then $M_{in} = \sum_R \sum_{h,m} D^{(2)}(R_{ih}) \, X_{hm} \, D^{(1)}(R^{-1}_{mn})$

$$= \sum D^{(2)}_{ih}(R) \, D^{(1)}_{mn}(R^{-1}) = 0 \quad \text{for any } i, h, m, n$$

If D is unitary: $D_{mn}(R^{-1}) = D^*_{nm}(R)$

then $\sum_R D^{(1)}_{ik}(R)\, D^{(2)*}_{nm}(R) = 0$.

If $D^{(1)} = D^{(2)}$: $M = \sum_R D^{(1)}(R) \times D^{(1)}(R^{-1})$

and $M D^{(1)}(S) = D^{(1)}(S) M$; from

~~theorem~~ two, $M = c\, 1$ (c depends on X).

$M_{in} = \sum_R D^{(1)}_{ik}(R)\, D^{(1)*}_{nm}(R) = c_{km} \delta_{in}$

$$\sum_n M_{nn} = \sum_n \sum_R D_{nk}\, D_{mn}(R^{-1})$$

$$= \sum_R \sum_n D_{mn}^{-1} D_{nk}$$

$$= \sum_R D_{mk}(R^{-1}R) = \sum_R \delta_{mk} = h\, \delta_{mk}$$

$$\text{or} = \sum_n c_{km} = c_{km}\, l_1$$

$$\therefore c_{km}\, l_1 = h\, \delta_{mk}$$

$$\therefore c_{km} = \delta_{km} \frac{h}{l_1} .$$

$$\therefore \sum_R D^{j}_{ik}(R)\, D^{(j')*}_{nm}(R) = \delta_{jj'}\, \delta_{in}\, \delta_{km} \frac{h}{l_j}$$

Nov 26 1940

Theorem concerning group representations:

$$\sum_R D^{(j)}_{\mu\nu}(R)\, D^{(j')}_{\rho\sigma}(R) = \delta_{jj'}\,\delta_{\mu\rho}\,\delta_{\nu\sigma}\,\frac{h}{l_j}.$$

h = no. of elements in group.
l_j = dimension of j. representation.

$$\sum_P c_j(P)\, c^*_{j'}(P) = \delta_{jj'}\, h.$$

Application of group theory is to problems having H with certain symmetry. eg: If $\psi(\underline{r})$ belongs to E, with V spherically symmetrical, then for any rotation P, $\psi(P\underline{r}) = \psi(\underline{r})$.

If operation P leaves Hamiltonian invariant, and $\psi(\underline{r})$ is sol'n of Schroedinger eq'n for energy E, then $\psi(P\underline{r})$ is a sol'n belonging to same energy; For:

$$H(r)\psi(\underline{r}) = E\,\psi(\underline{r}).$$

or $H(P\underline{r})\,\psi(P\underline{r}) = E\,\psi(P\underline{r})$

but $H(P\underline{r}) = H(\underline{r})$

$\therefore\ H(\underline{r})\,\psi(P\underline{r}) = E\,\psi(P\underline{r})$.

If degenerate, orthonormal sol'n's $\psi_\mu(\underline{r})$ for E:
$\mu = 1 \ldots l$:

Then $\psi_\mu(P\underline{r})$ is a sol'n corr. to E;
since ψ_μ's are complete set:

$$\psi_\mu(P\underline{r}) = \sum_\nu D_{\mu\nu}(P)\,\psi_\nu(\underline{r}).$$

D's give representation of symmetry group — i.e. of operators which leave Hamiltonian unchanged (they form a group since if $H(P\underline{r}) = H(\underline{r})$, $H(Q\underline{r})$ ...

e.g., group of rotations, for sph. symm. Hamiltonian;
permutation group, for Ham. of system with several electrons

$$\left[H = \frac{\sum p_i^2}{2m} + \sum \frac{e\,q}{r_i} + \sum_{ik} \frac{e^2}{r_{ik}} \right].$$

System in electric field: group of rotations about axis of field.
+ mirror image resp to plane containing field direction

" " magnetic " : group of rotations about axis
(but not mirror img in
+ mirror image w. resp. to plane ⊥ to field direction.

" " crystalline field : symmetry of crystal.

$D_{\mu\nu}(P)$ gives representation of group;

for: $\psi(PQ\,r) = \sum D_{\mu\nu}(PQ)\,\psi_\nu(r)$

$$= \sum_\rho D_{\mu\rho}(P)\,\psi_\rho(Q\,r) = \sum_{\rho\nu} D_{\mu\rho}(P)\,D_{\rho\nu}(Q)\,\psi_\nu(r)$$

$$\therefore\ D(PQ) = D(P)\,D(Q).$$

since there are l ψ_ν's, D is an l-dimensional representation of the group of the Hamiltonian.

If rep. is irreducible, need all l ψ's;
If rep. is reducible, ψ's fall into several sets, such that ψ's of each set only transform among themselves under symmetry operations.

Accidental degeneracy: if ψ's belonging to given E correspond to a reducible representation

e.g. : levels of alkali atom : ~~no degeneracy (disregard spin)~~ . n, l :

$(2l+1)$ ψ's , $m = -l, -l+1, \ldots, 0, \ldots, l-1, l$.

Transformation of ψ's under rot. corr. to irreducible

rep. of rotation group of dimension $2l+1$ (only one such rep.).

But H levels : n ; n^2 ψ's in ordered sets $l = 0, 1, \ldots n$

levels of same n & different l accidentally degenerate.

due to potential $1/r$

∴ H contains a feature which is purely accidental which no other

atom has - hence bad example of atom - alkali is better -

Disregarding accidental degeneracy, transformation of ψ's for

given E corr. to irreducible representation of group.

$$\psi_\mu (P\,1) \qquad \psi_\rho (P\,1) = \sum_\sigma D_{\rho\sigma}(P)\, \psi_\sigma(1)$$

$$\sum_P \psi_\mu(P\,1)\, \psi_\rho^*(P\,1) = \sum_{\nu\sigma} \sum_P D_{\mu\nu}(P)\, D^*_{\rho\sigma}(P)\, \psi_\nu \psi_\sigma^*$$

$$= \delta_{\mu\rho} \sum_{\nu\sigma} \delta_{\nu\sigma}\, \psi_\nu\, \psi_\sigma^*\, \frac{h}{l}$$

$$= \frac{h}{l}\, \delta_{\mu\rho} \sum_\nu |\psi_\nu|^2$$

Rotation : $\int \psi_m (P\,1)\, \psi_{m'}^* (P\,1)\, dP = 0$

Permutation : $\sum_{\text{Perm.}} \psi_\mu \psi_\rho^* = 0$

But if $\mu = \rho$: $\frac{1}{h} \sum_P |\psi_\mu|^2 (P\,1)$ = average over group elements $= \frac{1}{l} \sum_\nu |\psi_\nu|^2 (1)$. = average over ψ [illegible]

Nov. 28 | $\frac{1}{h}\sum_P |\psi_\mu(P\underline{r})|^2 = \frac{1}{l}\sum_\mu |\psi_\mu(\underline{r})|^2$!! ...

Suppose V is spherically symmetrical —

then group of Hamiltonian is group of all rotations in space

$\therefore \sum_m |\psi_{lm}(\underline{r})|^2$ is invariant against rotation (since by ... hand side ... also ...)

i.e. subshell charge density is spherically symmetrical.

(rare gases sph. symm.)

for J = 0, only one term on right, $\therefore$ $|\psi|^2$ is sph. symm. for singlet state.

Consider atom in cubically symmetrical field; (as Na in Na crystal -)

then average charge distrib. must have cubic symmetry -

Axial field : axially symmetrical $\sum_\mu |\psi_\mu|^2$

Inversion : $\underline{r} \to -\underline{r}$ average charge density invariant against inversion

If Ham. is invariant under both inversion & rotation -

$R I = I R$;

E	I	R
I	E	R'
R	R'	E

$\therefore$ E, I are a subgroup

E, R " "

If we have representation D(R), C(E, I),

$D(R)C(I) = D'(RI)$.

C : $E = 1$, $I = \{ {1 \atop -1} \}$ $D'(R) = D(R)$, $D'(E, I) = C(E, I)$.

$\therefore D'(RI) = \pm D(R)$.

inversion either changes sign of eigenf'ns, or leaves it alone.

parity - even or odd.

Rotation group: 1 irreducible representation of any dimension.

1 one dimensional: each element = 1.

1 2 - " : $j = \frac{1}{2}$ spinor transformation.

1 3 - " : $j=1$ $\cos\theta$ $\sin\theta e^{i\phi}$ $\sin\theta e^{-i\phi}$ or $x\ y\ z$:
gives transformation of coordinates —
& hence " " of any vectors.

1 4 - " : $j = 3/2$

1 5 - " : $j = 2$ Tensor transformation.

Wigner

&c.

$(2J+1)^{th}$ " rep : J

Value of J completely determines behavior of wave function of system under rotation

---

Permutations — many representations —

~~devion~~ Theorem says that sum over all ~~permutations~~ wave fns. of $\sum|\psi_n|^2$ must be ~~invariant~~ against permutation of electrons. ; hence it is symmetrical in all electrons.

(Pauli principle says this for whole f'n (space & spin) — but ~~this~~ tells us ~~that~~ space f'n also is symmetrical —)

Spin f'ns: 2 el., $\alpha(1)\alpha(2)$, $\alpha(1)\beta(2)+\alpha(2)\beta(1)$, $\beta(1)\beta(2)$ } $S=1$, transform like vector under rotation, ~~invariant~~ under permutation.

$\alpha(1)\beta(2)-\alpha(2)\beta(1)$ - $S=0$ - ~~invariant~~ under rotation antisym under permutation

Space f'n must have opposite symmetry as spin f'n, so that the product is antisym - for Pauli principle.

Very complicated for more than 2 el. —

With an external field, only axial symmetry, hence no. of group elements is reduced —

Consider matrices of element of restricted group in the representation of the original (sph.-symm.) group — It may be possible to find a ~~...~~ transformation reducing these —

e.g. if field is along z-axis; Hence only changes of azimuth permitted — Matrices of elements corresponding to rotation about z can be reduced to $\left| e^{im\varphi} \right|$ — & energy levels are split in field —

Nov. 30

H_0 original ~~Hamiltonian~~

H perturbed " ;

suppose the symmetry operations of H are a subgroup of sym. g. of H_0

Call P_0 the sym. operations of H_0

P " " " H.

Representation $D(P_0)$, $D(P)$. $\underline{l}$ state of energy $\underline{E}$.

Perhaps $D(P)$ is reducible :

$$S^{-1} D S = D'(P)$$

Where $D'_{jk}(P) \neq 0$ only if j & k belong to same subset of no's (...)

D' : $\begin{pmatrix} & 0 & 0 & \\ 0 & & 0 & 0 \\ 0 & 0 & & 0 \end{pmatrix}$ then in field H, only the eigenf'n's belonging to little ~~diagonal~~ ... degenerate

i.e. level E_0 is split up into several different E-values, corresponding to sets of degenerate ψ's of D'; by the perturbation
↳ irreducible representations of group of H —

example:

In homogeneous el. field;

rotations about field axis
reflections of plane thru field

reflection : $e^{im\varphi} \rightarrow e^{-im\varphi}$

$e^{im\varphi}$, $e^{-im\varphi}$ belong to same representation of group

$$\text{Rotation about } \varphi_0 : \quad D = \begin{pmatrix} e^{im\varphi} & 0 \\ 0 & e^{-im\varphi} \end{pmatrix}.$$

$$\text{Reflection} : \quad D = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

$m = 0$, 1 dimensional representation.
$m \neq 0$, 2 " " .

If H_0 is invariant against rotation about origin:

$$P_l^m(\theta) e^{im\varphi}.$$

$$D \begin{matrix} m=0 \\ m=1 \\ m=-1 \\ = \end{matrix} \begin{pmatrix} \times & & & & & \\ & \times & \times & & & \\ & \times & \times & & & \\ & & & \times\ \times & \times & \\ & & & \times\ \times & & \\ & & & \times & \times\ \times & \\ & & & & \times\ \times & \\ & & & & & \text{etc.} \end{pmatrix}$$

(reduced into irreducible representations of group of perturbation H)

e.g. if $l = 3$, splits into 4 levels, each corr. to $|m| = 0, 1, 2, 3$.

Group theory gives these results for any magnitude of perturbation —

Electric field: perturbation F_z;

matrix element of perturbation: $\int \psi_m^* F z \, \psi_n = 0$ if ψ_m & ψ_n have same parity.

∴ el. field has vanishing matrix elements between degenerate states;

to get the splitting, have to take 2nd order approximation. hence one wonders whether further approx. makes further change; but group theory tells me at once what splitting there is.

Magnetic field:

Symmetry ~~operations~~:

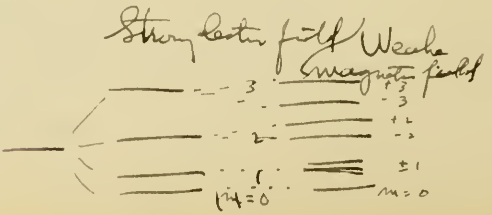
Rotation about field.

Reflection at plane ⊥ to field: $\theta \to \pi - \theta$.

↳ $P_l^m(\theta) \to (-1)^{l-m} P_l^m(\theta)$.

all matrix elements of perturbation exist, get $2l+1$ levels: $D(P) = \begin{pmatrix} \times & & & \\ & \times & & \\ & & \times & \\ & & & \ddots \end{pmatrix}$ one irreducible representation for each value of m

~~Strong~~



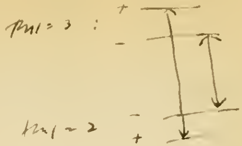
$\Delta E = H \mu g m$.

This sometimes [illegible] in crystals –

inversion of one level in salts of rare earth . .

much bigger shift

than normal —



It is important to know what irreducible representations are contained in the reducible parts of a representation — (as above). In general, don't know & can't use wave function (like P_l^{m}'s above).

$$\sum_P D^j_{\mu\nu}(P)\, D^{j'*}_{\rho\sigma}(P) = \delta_{jj'}\,\delta_{\mu\rho}\,\delta_{\nu\sigma}\,\frac{h}{l_j}$$

Consider an h-dimensional space; whose axes correspond to group elements $P_{1,2,\ldots}$ hence find a pt. corresponding to $D^j_{\mu\nu}(P)$ (coord of pt. are values of $D^j_{\mu\nu}$ for each P) Then $D^j_{\mu\nu}(P)$ is an h-dimensional vector; one vector for each (j, μ, ν). and above theorem simply says these vectors are orthogonal —

For a given j, (l_j^2) vectors (l_j values of μ & ν).

∴ a sum over j gives $\sum_j l_j^2 \leq h$, since we can't have more than h orthogonal vectors — ∴ no. of representations is limited, for a finite group.

class c: $\quad X^{-1} C_i^{(k)} X = C_j^{(k)} \quad$ X any element of group —

p classes. then $D(X^{-1})\, D(C_i^{(k)})\, D(X) = D(C_j^{(k)})$.

We know that spur P remains invariant under similarity transformation; spur $D = \sum_\mu D_{\mu\mu}(C^h)$.

∴ spur remain the same for all elements of class

call spur the character of representation $\chi(C)$.

character is the same for all element of one class.

∴ can use character ~~set~~ of ~~classes~~ elements to specify ...

(e.g. cubic group, 48 elements, 10 classes).

~~Nov~~ 3 Dec. character $\chi(C) = \sum_k D^j_{kk}(P)$. is the same for all elements of a class.

Orthogonality: $\sum_P D^j_{\mu\nu}(P)\, D^{j'\,*}_{\rho\sigma}(P) = \delta_{jj'}\delta_{\mu\rho}\delta_{\nu\sigma}\frac{h}{l_j}$

Now $\sum_P \chi_j(P)\chi^*_{j'}(P) = \sum_P \sum_k \sum_l D^j_{kk}(P)\, D^{j'\,*}_{ll}(P) = \delta_{jj'}\frac{h}{l_j} \cdot$

$= \delta_{jj'}h$.

if n_K is no of group elements in class C_K:

$$\sum_k \frac{n_k}{h}\chi_j(C_k)\chi^*_{j'}(C_k) = \delta_{jj'}$$

∴ $\sqrt{\frac{n_k}{h}}\chi_j(C_k)$ is a vector in class-space; p-dimension - p classes

there can not exist more than p ~~orthogonal vectors~~

∴ no. of representations $\leq$ no. of classes — !

Before we had $\sum_j l_j^2 = h$.

We multiplied classes: $C_k C_l = \sum_m a_{klm} C_m$ + got other classes various no.'s of times –

Consider the quantity $\sum_{P \subset C_k} D^j(P)$; it must commute with all matrices of the group; for $X^{-1} C_k^\nu X = C_k^\mu$

$\therefore C_k^\nu X = X C_k^\mu$ if ν covers all element of class, so does μ;

$$\therefore X \sum_{P \subset C_k} D^j(P) = \sum_{P \subset C_k} D^j(P)\, X$$

$$\therefore \sum_{P \subset C_k} D^j(P) = c\,1 \quad \text{a multiple of unit matrix.}$$

Now $\sum_n \sum_{P \subset C_k} D^j_{nn}(P) = n_k \chi_j(C_k)$

but also $\sum_n \sum_{P \subset C_k} D^j_{nn}(P) = c \sum_n 1 = c\, l_j$

$$\therefore c\, l_j = n_k \chi_j(C_k).$$

$$\therefore c = \frac{n_k \chi_j(C_k)}{l_j}$$

Now $D^j(P) D^j(Q) = D^j(PQ)$.

$$\sum_{P \subset C_k} \sum_{Q \subset C_l} D^j(P) D^j(Q) = \sum_{P,Q} D^j(PQ) = \sum_m a_{klm} \sum_{R \subset C_m} D^j(R)$$

$\downarrow$

$$\frac{n_k n_l \chi_j(C_k)\chi_j(C_l)}{l_j^2} = \sum a_{klm} \frac{n_m \chi_j(C_m)}{l_j}$$

but $\chi_j(E) = l_j$: $\quad \therefore n_k n_l \chi_j(C_k)\chi_j(C_l) = \sum_m a_{klm} n_m \chi_j(C_m) \chi_j(E)$

Reducible representation $= \Sigma\, b_j\, D^j$ (i.e. rep. D^j occurs b_j times in the reducible representation)

then $\chi(C_k) = \sum_j b_j \chi_j(C_k)$

and $\sum_k n_k \chi_{j'}^*(C_k) \chi(C_k) = \sum_k \sum_j b_j\, n_k\, \chi_{j'}^*(C_k)\, \chi_j(C_k)$

$= \sum_j \delta_{jj'}\, b_j\, h = b_{j'}\, h$.

$\therefore b_j = \frac{1}{h} \sum_k n_k\, \chi_{j'}^*(C_k)\, \chi(C_k)$.

Regular ~~Representation~~

suppose $PQ = R$.

suppose h rows & columns; $Q \cdot \cdot \begin{pmatrix} \cdot & 0 & \overset{R}{1} & 0 \end{pmatrix}$

$E = 1$;

$P \neq E$ has no diagonal elements.

show that this is a representation:

if we have two elements P, P':

$(PP')_{QR} = \sum_S P_{QS} P'_{SR} = \sum_S \delta_{S,PQ}\, \delta_{R,P'S} = \delta_{R,P'PQ} = 1$ if $R = P'PQ$ or

Reg. Rep: $\chi(E) = h$,

$\chi(C_k) = 0$ for $C_k \neq E$.

[illegible] $\chi_j^*(E) = l_j$; $\therefore$ reg. rep. contains [illegible]

$\therefore$ Reg. Rep. $D_r = \sum \ell_j D^j$

Dec 5. We were proving: $\sum_j \ell_j^2 = h$

No. of representations = p. no. of classes.

Had found that regular rep. contains each irreducible representation ℓ_j times: $D_r = \sum \ell_j D^j$.

Got that from expansion theorem: no. of times a given rep. occurs, b_j is given by: $b_j = \frac{1}{h} \sum_k n_k \chi_j^*(C_k)\chi(C_k)$ (given reducible)

Regular rep: $\chi(E) = h$

$\chi(P) = 0, \quad P \neq E.$

whence $b_j = \chi_j(E) = \ell_j$

Now $\sum_P |\chi(P)|^2 = \sum_{P j j'} b_j \chi_j(P) b_{j'} \chi_{j'}^*(P)$.

$= \sum_{jj'} b_j b_{j'} \sum_P \chi_j(P)\chi_{j'}^*(P)$

$= \sum_j |b_j|^2 h$

smallest possible value of $\sum |\chi(P)|^2$ is h.

if this is so, the rep. is irreducible for then one $b_j = 1$, others 0.

For a regular rep.: $b_j = \ell_j$, and $h \sum |\ell_j|^2 = \sum_P |\chi(P)|^2$

$= h^2$

[illegible] $\sum |\ell_j|^2 = h$

Now $\sum_j \chi_j(C_h)\, l_j = 0$ when $C_h = E$?

$$\sum_j \chi_j(E)\,\chi_j(C_h) = n\,\delta_{h,1} \qquad \text{if } C_1 = E .$$

since $l_j = \chi_j(E)$ for regular repn.

We had:

$$n_k n_l\, \chi_j(C_k)\,\chi_j(C_l) = l_j \sum_m a_{klm}\, n_m\, \chi_j(C_m)$$

sum over j:

$$n_k n_l \sum_j \chi_j(C_k)\,\chi_j(C_l) = \sum_m a_{klm}\, n_m \sum_j l_j\, \chi_j(C_m)$$

$$= \sum_m a_{klm}\, n_m\, \delta_{m,1}\, n$$

$$= a_{kl1}\, n, \qquad n_1 = 1 .$$

Take an element X_k of class C_k.

X_k^{-1} belongs to a class C_{-k}, say.

and all X_i^{-1} belong to same class C_{-k}.

also all inverses of elements of C_{-k} belong to C_k.

Now $C_k C_{-k}$ gives E n_k times + other ones:

$$C_k C_{-k} = n_k E + \cdots$$

$$\therefore a_{kl1} = \begin{cases} n_k & \text{if } l = -k \\ 0 & \text{otherwise.} \end{cases}$$

Now $D(X)_h \; D(X_h^{-1}) = 1$

D is unitary ; $\therefore D^{-1} = \tilde{D}^*$

$D^{-1}_{\mu\nu} = D^*_{\nu\mu}$

$\therefore \chi(X_h^{-1}) = \chi^*(X_h)$

if a class is its own inverse, it must have a real character ; otherwise, it is the complex conjugate ..

$$\therefore \; n_h \sum_j \chi_j^*(C_\ell)\, \chi_j(C_h) = \delta_{h\ell}\, h .$$

(since $n_h n_\ell \sum \chi_j(C_h) \chi_j(C_\ell) = a_{h\ell,1}\, h = \delta_{\bar{h},\ell}\, n_h\, h$

$$\therefore \; n_\ell \sum \chi_j(C_{-h})\, \chi_j(C_\ell) = \delta_{h\ell}\, h .$$

new orth. rel: $\quad$ or $\; n_\ell \sum_j \chi_j^*(C_h)\, \chi_j(C_\ell) = \delta_{h\ell}\, h$.

Orth. rel. no 1 : χ_j is a vector in class-space of p-dimensions

$\therefore$ the no. g. of irreducible reps. is $g \le p$.

Orth. rel. no 2 : $\chi_j(C_h)$ is vector in representation-space of g-dimensions

$\therefore$ the no p. of classes is $p \le g$;

$\therefore p = g$.

i.e. no. of irreducible reps. of group = no. of classes.

Example : cubic group : 48 elements, 10 classes.

Pure rotations :	24 "	5 "
Inversion × :	24 "	5 "

∴ 5 representations of pure rotation group –

and $\Sigma l_j^2 = 24$

∴ $2 \cdot 3^2 + 1 \cdot 2^2 \cdot 2 \cdot 1^2$

∴ 2 3-dim. rep. non-equivalent
1 2-dim " " "
2 1-dim " " "

Consider group E, I : 2 rep: $\rightarrow \begin{cases} E & I \\ 1 & 1 \\ 1 & -1 \end{cases}$.

& get whole group from

this & rotation group.

	E	C_2	C_3	C_4	C_5
op	identity	rot. thru π about cubic axis	rot. thru π/2 about cubic axis	rot thru π about face diagonal	rot. thru 2π/3 about space diagonal
nh :	1	3	6	6	8

each class is its own inverse

∴ real character.

Find characters of classes. Ann d. Phys. 3 (190?)

get 5 representations Γ_{12345}.

Γ_1	1	1	1	1	1
Γ_2	1	1	-1	-1	1
Γ_3	2	2	0	0	-1
Γ_4	3	-1	1	-1	0
Γ_5	3	-1	-1	1	0

Doc. 7.

~~E C₂ C₃ C₄ C₅~~

$$P_l^m(\theta)\, e^{im\varphi}$$

rotate thru φ_0: multiply by $e^{im\varphi_0}$.

then $\chi(\varphi_0) = \sum_{m=-l}^{l} e^{im\varphi_0} = \dfrac{\sin(l+\frac{1}{2})\varphi_0}{\sin \varphi_0/2}$.

cubic group is subgroup of rotation group; can get it by rotation about particular axes; above expression is OK for any axis. We had rotations:

	E	C_2	C_3	C_4	C_5
φ_0 =	0	π	$\pi/2$	π	$2\pi/3$
$\chi(\varphi_0)$:	$2l+1$	$(-1)^l$	$+1$ $l = 4n, 4n+1$; -1 $l = 4n+2, 4n+3$	$(-1)^l$	$+1$, $l = 3n$; 0 $l = 3n+1$; -1 $l = 3n+2$

$\therefore \chi_l(C_k) = \sum b_{lj}\, \chi_j(C_k)$.

rotation group. ⌊ irreducible cubic character

	$\chi_l(E)$	$\chi_l(C_1)$	$\chi_l(C_3)$	$\chi_l(C_4)$	$\chi_l(C_5)$	
$l=0$	1	1	1	1	1	$\longrightarrow \Gamma(1)$
1	3	−1	1	−1	0	$\longrightarrow \Gamma(4)$
2	5	1	−1	1	−1	$\longrightarrow \Gamma(3) + \Gamma(5)$
3	7	−1	−1	−1	1	$\longrightarrow \Gamma_2 + \Gamma_4 + \Gamma_5$
4	9	1	1	1	0	$\longrightarrow \Gamma_1 + \Gamma_3 + \Gamma_5 + \Gamma_5$
5	11	−1	1	−1	−1	$\longrightarrow$
6	13	1	−1	1	1	

etc.

$\therefore$ $l(\alpha j) = 0, 1$, no splitting of s, p. levels in cubic field

$j = 2, 3, 4$ split into 2, 3, 4 levels; $j = 5, 6$, 4, 6 levels.

Rare-earth salts show this splitting —
incomplete 4-f shells.

4-f shell is low in atom, not much disturbed when atom is put in crystal. It gives rise to rather complicated angular momenta; get levels corresponding to large j due to internal electrons; if it were external ones, would be used up in union of bonds; (e.g.

H - H	½	0
½ - ½	0	
N - N	N	
3/2 3/2	0	

chemical forces always try to put spin anti-parallel)

But when large ang. mom. is due to internal electrons, it doesn't interact w. neighboring atoms. 4f electrons are subject to a field of crystal; if it is cubic, get splitting as predicted. But analysis is difficult, because of lack of knowledge of states (intermediate coupling — several 4f electrons — figure out levels!)

Van-Vleck — magnetic effects — usually in agreement.

Multiplication of ~~Representations~~.

Imagine two electrons: $Y_{l_1 m_1}(\theta_1 \varphi_1)\, Y_{l_2 m_2}(\theta_2 \varphi_2)$.

Describe atom by product of such $\Im$ f'ns.

rotation leaves ~~interaction~~ between electrons unchanged

∴ want to know representation which leaves product f'ns unchanged

Suppose we have representations D_1, D_2 for electrons;

Represent by $D_1 \times D_2$, representation of product fns —
each elt of product matrix is obtained by multiplying one
elmt of D_1 by one of D_2. $j_1 j_2$ rows + columns.

$$\chi = \sum_{\rho\sigma} D^{(1)}_{\rho\rho} D^{(2)}_{\sigma\sigma} = \chi^{(1)} \chi^{(2)}$$

here $$\chi^{(1)}\chi^{(2)} = \sum_{m_1=-l_1}^{l_1} \sum_{m_2=-l_2}^{l_2} e^{im_1\phi_1 + im_2\phi_2} \qquad m = m_1 + m_2$$

$$= \sum_{L=|l_1-l_2|}^{l_1+l_2} \sum_{m=-L}^{L} e^{-im\phi}$$

∴ the reducible representation generated by product splits up into irreducible representations;

$$= \sum_{L=|l_1-l_2|}^{l_1+l_2} \chi_L$$

reads split into terms for $|l_1-l_2| \dots l_1+l_2$

Optical transition probabilities —

$$\int z\, \psi_{i\mu}\, \psi^*_{f\nu}\, d\tau$$

Can rotate all three factors simultaneously —

z transforms according to $D^{(1)}$

$\psi_{i\mu}$ " " $D^{(l)}$

$\psi_{f\nu}$ " " $D^{(l')}$.

then $D^{(1)} \times D^{(l)} \times D^{(l')} = D^0 +$ others

This can be only if $D^{(1)} \times D^{(l)}$ contains $D^{(l')}$.

this only if $l' = l \pm 1, l$ — trivial

for ~~sphere~~ rotating prop. but not for cubic.

Do something about —

Dec. 15. 1940

Dirac Relativistic Equation: P.R.S. 1927.

The ~~relativistic~~ Schroedinger eq'n (also Klein Gordon) -

Use: $E = V + \frac{p^2}{2m}$ for ordinary mech:

then: $i\hbar \frac{\partial}{\partial t} \psi = \{ V + (-\frac{\hbar^2}{m}) \Delta \} \psi$.

E: $i\hbar \frac{\partial}{\partial t}$

p_x: $-i\hbar \frac{\partial}{\partial x}$

etc.

~~with~~ group vel.

particle vel:

$e^{\frac{i}{\hbar}(p \cdot r - Et)}$

Relativistic mechanics:

$(W-V)^2 = c^2 p^2 + m^2 c^4$ m rest ma

$W = E + mc^2$.

then: $(i\hbar \frac{\partial}{\partial t} - V)^2 \psi + c^2 \hbar^2 \Delta \psi - m^2 c^4 \psi = 0$

For electromagnetic field: $p \to p - \frac{e}{c} A$.

then:

K. G.

$\{ (i\hbar \frac{\partial}{\partial t} - V)^2 - c^2(-i\hbar \,\underline{\text{grad}} - \frac{e}{c} \underline{A})^2 - m^2 c^4 \} \psi = 0$

Contains 2nd derivative of time.

then $\frac{\partial^2 \psi}{\partial t^2} = O\psi + P \frac{\partial \psi}{\partial t}$.

$\therefore$ must give not only ψ but also $\dot\psi$ to get $\ddot\psi$.

whereas ordinary wave mech., give only ψ, & get $\dot\psi$ -

This has as consequence that energy is no longer positive definite

for a known wave f'n gives $\pm (W-V)$ for energy -

$W - V = \pm\sqrt{c^2p^2 + m^2c^4}$.

This was bad — in fact charge densities weren't + definite either. [In fact, here $\psi^* \frac{\partial \psi}{\partial t} - \psi \frac{\partial \psi^*}{\partial t} = \rho$, $\underline{j} = \psi^* \operatorname{grad}\psi - \psi \operatorname{grad}\psi^*$

$\rho, \underline{j}$ form a 4-vector

ρ may be + or − . This, Dirac said, ~~contradicts~~ experience — (no positrons known then) —

also, spin wasn't very well taken care of — hence he looked for another equation — which would give a definite sign for charge density, like non-rel. Schr. theory. in which $\rho = \psi\psi^*$

Hence any theory which gives ρ as $\Sigma\, \psi^*\psi$ will be OK — but not if it has derivatives.

∴ Dirac postulates ~~that~~ (ρ also of this sort) ; only possible if eq'n. has only 1st time derivatives occurs.

But in relat. theory, time + space coords enter in same way — hence only 1st order space derivatives as well.

Now in E.M. theory, we have wave eq'n :

$$\nabla^2 E - \frac{1}{c^2}\frac{\partial^2 E}{\partial t^2} = 0$$

K.G. eq'n with $V = 0$:
$$\nabla^2\psi - \frac{1}{c^2}\frac{\partial^2 \psi}{\partial t^2} = \left(\frac{mc}{\hbar}\right)^2 \psi .$$

But in E.M. case, we have Maxwell's eq'ns :

(field free space) $\quad \frac{1}{c}\dot{H} = -\nabla \wedge E$, $\quad \frac{1}{c}\dot{E} = \nabla \wedge H$ — 1st order eqns — hence just like was Dirac ~~wanted~~ —

But each Maxwell eq'n connects different components (E, H).

3 components in each eq'n). $w = \frac{1}{8\pi}(E^2 + H^2) = \frac{1}{8\pi}\sum_{\kappa=1}^{6} \psi_\kappa^2$ – ✗

this form we want for charge density –

I introduce wave f'n of several component, ψ_κ

In general, we might have:

$$\frac{1}{c}\frac{\partial \psi_\kappa}{\partial t} = \sum_\lambda a^x_{\kappa\lambda}\frac{\partial \psi_\lambda}{\partial x} + a^y_{\kappa\lambda}\frac{\partial \psi_\lambda}{\partial y} + a^z_{\kappa\lambda}\frac{\partial \psi_\lambda}{\partial z}$$

Connecting components of ψ

$$+ \frac{mc}{\hbar} \cdot b_{\kappa\lambda}\psi_\lambda \,;$$

or: $$\frac{1}{c}\frac{\partial \psi_\kappa}{\partial t} = \left(a^x\frac{\partial \psi}{\partial x} + a^y\frac{\partial \psi}{\partial y} + a^z\frac{\partial \psi}{\partial z}\right)_\kappa + \frac{mc}{\hbar}(b\psi)_\kappa$$

also put i in (latter)

$$= (\underline{\alpha} \cdot \text{grad}\,\psi)_\kappa + \frac{imc}{\hbar}(b\psi)_\kappa \,.$$

or: $$\frac{1}{c}\frac{\partial \psi}{\partial t} = \underline{\alpha}\cdot\text{grad}\,\psi + i\frac{mc}{\hbar}b\psi \,.$$

This must give K-G. eq'n when squared –

$$\frac{1}{c^2}\frac{\partial^2 \psi}{\partial t^2} = \left(\underline{\alpha}\cdot\text{grad} + i\beta\frac{mc}{\hbar}\right)^2\psi$$

$$= \Big\{\alpha_x^2\frac{\partial^2}{\partial x^2} + \alpha_y^2\frac{\partial^2}{\partial y^2} + \alpha_z^2\frac{\partial^2}{\partial z^2} - \beta^2\frac{m^2c^2}{\hbar^2}$$

$$+ (\alpha_x\alpha_y + \alpha_y\alpha_x)\frac{\partial^2}{\partial x\partial y} + \dots\Big\}\psi.$$

$$+ \alpha_x\beta + \beta\alpha_x\frac{\partial}{\partial x} + \dots$$

this is K. G. -eq'n if we

have: $\alpha_x^2 = \alpha_y^2 = \alpha_z^2 = \beta^2 = 1$,

$$\alpha_x\alpha_y + \alpha_y\alpha_x = 0$$

$$\alpha_x\alpha_z + \alpha_z\alpha_x = 0$$

$$\alpha_y\alpha_z + \alpha_z\alpha_y = 0$$

$$\alpha_x\beta + \beta\alpha_x = 0$$

Dec 12

if $\begin{cases} \alpha_i \alpha_k + \alpha_k \alpha_i = 2\delta_{ik} \\ \alpha_i \beta + \beta \alpha_i = 0 \quad \beta^2 = 1 \end{cases}$

then $\frac{1}{c}\frac{\partial \psi}{\partial t} = \left(-\underline{\alpha}\cdot \underline{\text{grad}} + \frac{imc}{\hbar}\beta\right)\psi$ → analogue to Maxwell eq'n.

gives $\frac{1}{c^2}\frac{\partial^2 \psi}{\partial t^2} = \left(\nabla^2 - \frac{m^2c^2}{\hbar^2}\right)\psi$ → analogue to wave eq'n

How many rows & columns for α's & β's ?

Look at $\alpha_i\alpha_k + \alpha_k\alpha_i = 2\delta_{ik}$: these we had before, for the spin matrices : $\underline{\sigma} = \begin{pmatrix} \underline{k} & \underline{i} - i\underline{j} \\ \underline{i}+i\underline{j} & -\underline{k} \end{pmatrix}$.

e.g.: $\sigma_x\sigma_y = i\sigma_3$ $\quad\therefore \sigma_x\sigma_y + \sigma_y\sigma_x = 0$.
$\sigma_y\sigma_x = -i\sigma_3$ etc.

also $\sigma_i^2 = 1$;

∴ spin matrices would work, if we had only α constants;
but must have a β which anticommutes with all three;

There is no 4th 2 row matrix which commutes with all of these - (for these three with unit matrix form a complete set) -

try iterating σ's ; ∴ 4 row matrices:

~~e.g.~~: $\alpha_x : \begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix}$ $\alpha_y : \begin{pmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{pmatrix}$ $\alpha_3 : \begin{pmatrix} 0 & \sigma_3 \\ \sigma_3 & 0 \end{pmatrix}$

these still anticommute -

$\alpha_x\alpha_y = \begin{pmatrix} \sigma_x\sigma_y & 0 \\ 0 & \sigma_x\sigma_y \end{pmatrix}$ etc.

another which anticommutes with all of α's is $\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

$\alpha_x\alpha_y + \alpha_y\alpha_x : \begin{pmatrix} \sigma_x\sigma_y + \sigma_y\sigma_x & 0 \\ 0 & \sigma_x\sigma_y + \sigma_y\sigma_x \end{pmatrix}$

$\alpha_x\beta : \begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} 0 & -\sigma_x \\ \sigma_x & 0 \end{pmatrix}$ ∴ anticomm

etc. $= 0$

$\beta\sigma_x = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix} = \begin{pmatrix} 0 & \sigma_x \\ -\sigma_x & 0 \end{pmatrix}$

Therefore ψ has 4 components — $\begin{pmatrix}\psi_1\\ \psi_2\\ \psi_3\\ \psi_4\end{pmatrix}$ $(\psi_1^*\ \psi_2^*\ \psi_3^*\ \psi_4^*)$

$$\alpha_x = \begin{pmatrix}0&0&0&1\\0&0&1&0\\0&1&0&0\\1&0&0&0\end{pmatrix} \qquad \alpha_y = \begin{pmatrix}0&0&0&-i\\0&0&i&0\\0&-i&0&0\\i&0&0&0\end{pmatrix}$$

$$\alpha_z = \begin{pmatrix}0&0&1&0\\0&0&0&-1\\1&0&0&0\\0&-1&0&0\end{pmatrix} \qquad \beta = \begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{pmatrix}$$

$\therefore$

$$\frac{1}{c}\frac{\partial \psi_1}{\partial t} = -\frac{\partial \psi_4}{\partial x} + i\frac{\partial \psi_4}{\partial y} - \frac{\partial \psi_3}{\partial z} + \frac{imc}{\hbar}\psi_1$$

$$\frac{1}{c}\frac{\partial \psi_2}{\partial t} = -\frac{\partial \psi_3}{\partial x} - i\frac{\partial \psi_3}{\partial y} + \frac{\partial \psi_4}{\partial z} + \frac{imc}{\hbar}\psi_2$$

$$\frac{1}{c}\frac{\partial \psi_3}{\partial t} = -\frac{\partial \psi_2}{\partial x} + i\frac{\partial \psi_2}{\partial y} - \frac{\partial \psi_1}{\partial z} - \frac{imc}{\hbar}\psi_3$$

$$\frac{1}{c}\frac{\partial \psi_4}{\partial t} = -\frac{\partial \psi_1}{\partial x} - i\frac{\partial \psi_1}{\partial y} + \frac{\partial \psi_2}{\partial z} - \frac{imc}{\hbar}\psi_4$$

or, if $\psi_j \sim e^{-\frac{iE}{\hbar}t}$

$$-\frac{i}{\hbar c}\left[E + mc^2\right]\psi_1 = \frac{\partial \psi_4}{\partial x} - i\frac{\partial \psi_4}{\partial y} + \frac{\partial \psi_3}{\partial z}$$

$$\text{''}\qquad \psi_2 = \frac{\partial \psi_3}{\partial x} - i\frac{\partial \psi_3}{\partial z} - \frac{\partial \psi_4}{\partial z}$$

$$-\frac{i}{\hbar c}\left[E - mc^2\right]\psi_3 = \frac{\partial \psi_2}{\partial x} - i\frac{\partial \psi_2}{\partial y} + \frac{\partial \psi_1}{\partial z}$$

$$\text{''}\qquad \psi_4 = \frac{\partial \psi_1}{\partial x} + i\frac{\partial \psi_1}{\partial z} - \frac{\partial \psi_2}{\partial z}$$

Non-rel. limit, $E - mc^2 \ll mc^2$, $\psi_1, \psi_2 \ll \psi_3\ \psi_4$

In non-relativistic approx, get Schrödinger eq'n, in field free case — with field, get Pauli eq'n's.

Investigate relativistic invariance —

Read Pauli's article, Handbuch 24/1.

Relativistic invariance means that the form

) the equation remains the same when making a Lorentz transformation or rotation (but various components transform into each other).

i.e. if S' moves with respect to S with unit vel., then we want to have:

$$\frac{1}{c}\frac{\partial \psi'}{\partial t'} = \left(-\alpha \cdot \mathrm{grad}' + \frac{imc}{\hbar}\beta\right)\psi'$$

when ψ' is linear fn of ψs —

Invariance is proven if we can write down $\psi'_\lambda = \sum_\lambda a_{\kappa\lambda}\psi_\lambda$

Pauli does this — using infinitesimal Lorentz transformation.

(in this case, get $a_{\kappa\lambda} = \delta_{\kappa\lambda} + \epsilon\alpha\,\beta_{\kappa\lambda}$ etc —

Ex. 17. Dirac: $\frac{1}{c}\dot{\psi} + \underline{\alpha}\cdot\text{grad}\,\psi - \frac{imc}{\hbar}\beta\psi = 0$ $\quad \psi^* \rightarrow$ multiply

$\frac{1}{c}\dot{\psi}^* + \alpha^*\cdot\text{grad}\,\psi^* + \frac{imc}{\hbar}\beta^*\psi^* = 0 \quad \leftarrow \psi$ & add.

$$\frac{1}{c}(\psi^*\dot{\psi} + \dot{\psi}^*\psi) + \psi^*\alpha\cdot\text{grad}\,\psi + \alpha^*\cdot\text{grad}\,\psi^*\,\psi - \frac{imc}{\hbar}(\psi^*\beta\psi - \beta^*\psi^*\psi)$$

But $\psi^*\alpha_x\frac{\partial\psi}{\partial x} = \sum_\kappa \psi^*_\kappa\left(\alpha_x\frac{\partial\psi}{\partial x}\right)_\kappa = \sum_{\kappa\lambda}\psi^*_\kappa\,\alpha^x_{\kappa\lambda}\frac{\partial\psi_\lambda}{\partial x}$.

$\alpha^*_x\frac{\partial\psi^*}{\partial x}\cdot\psi = \sum_{\kappa\lambda}\alpha^{*x}_{\kappa\lambda}\frac{\partial\psi^*_\kappa}{\partial x}\psi_\lambda = \frac{\partial\psi^*}{\partial x}\tilde{\alpha}^*\psi$

$\therefore (\alpha^*\cdot\text{grad}\,\psi^*)\psi = (\text{grad}\,\psi^*\cdot\tilde{\alpha}^*)\psi$

and $\beta^*\psi^* = \psi^*\tilde{\beta}^*$

$$\therefore \frac{1}{c}(\psi^*\dot{\psi} + \dot{\psi}^*\psi) + \psi^*\alpha\cdot\text{grad}\,\psi + \text{grad}\,\psi^*\cdot\tilde{\alpha}^*\psi - \frac{imc}{\hbar}(\psi^*\beta\psi - \psi^*\tilde{\beta}^*\psi)$$

~~$\frac{1}{c}\frac{\partial(\psi^*\psi)}{\partial t}$~~

To get continuity eqn, must have term without derivative vanish, i.e. $\beta = \tilde{\beta}^*$. Hermitean

If further, $\alpha = \tilde{\alpha}^*$,

we have:

$$\frac{1}{c}\frac{\partial(\psi^*\psi)}{\partial t} + \text{div}\,\psi^*\underline{\alpha}\psi = 0.$$

$\therefore \psi^*\psi = \rho$: charge density

$\therefore c(\psi^*\underline{\alpha}\psi) = \underline{j}$: current density.

Now $\dot{A} = \frac{i}{\hbar}(HA - AH)$.

In Dirac theory: $H = -i\hbar c\,\underline{\alpha}\cdot\text{grad} - mc^2\beta$
$= c\,\underline{\alpha}\cdot\underline{p} - mc^2\beta$

if $A = q$: $HA - AH = c\,\underline{\alpha}\cdot\underline{p}\,q - mc^2\beta q - qc\,\underline{\alpha}\cdot\underline{p} + mc^2\beta q$

$$HA - AH = -[\alpha_q p_q q - \alpha_q q p_q] = -i\hbar c\,\alpha_q$$

$$\therefore \quad \dot{q} = \frac{i}{\hbar}[HA - AH]$$

$$= \frac{i}{\hbar}\cdot -i\hbar c\,\alpha_q = c\,\alpha_q .$$

$$\therefore \quad \dot{q}_{mn} = c(\alpha_q)_{mn} = c\int \psi_m^* \alpha_q \psi_n \, d\tau = \frac{i}{\hbar}(E_m - E_n) x_{mn}$$

External fields : — $E^2 = c^2 p^2 + m^2 c^4$

$$\downarrow \qquad \searrow$$

$$(E - V)^2 = c^2\left(p + \tfrac{e}{c}A\right)^2 + m^2 c^4$$

and $H = V + c\,\alpha\cdot\left(p + \frac{e}{c}A\right) - mc^2\beta$.

$$= V + \alpha\cdot(cp + eA) - mc^2\beta .$$

$$\therefore \quad \frac{1}{c}\frac{\partial \psi}{\partial t} = -\frac{i}{\hbar c}V\psi - \alpha\cdot\text{grad}\,\psi - \frac{ie}{\hbar c}\alpha\cdot A\psi - \frac{imc}{\hbar}\beta\psi .$$

Nothing is changed in previous derivation of continuity eq.

(if V, A are real) still have $\rho = \psi^*\psi$
$j = \psi^* \alpha\, \psi$

likewise, still have $\dot{q} = c\,\alpha_q$.

Now $\dot{p}_q = \frac{i}{\hbar}(H p_q - p_q H)$

$$= \frac{i}{\hbar}\left(H\frac{\partial}{\partial q} - \frac{\partial}{\partial q}H\right)\cdot -i\hbar$$

$$= -\frac{\partial}{\partial q}(V + e\,\alpha\cdot A) \qquad \text{as in classical mech.}$$

~~$m\ddot{q} = \dot{p}_q + \frac{e}{c}\dot{A}_x$~~

F wld free : $e^{-i/\hbar \ldots}$:

$$\psi^*\alpha_x \,|\, E\psi = c\underline{\alpha}\cdot\underline{p}\,\psi - mc^2\beta\psi$$

$$E\psi^* \;\; - \overset{*}{p}\psi^*\cdot\alpha - \psi^* mc^2\beta \,|\, \alpha_x\psi$$

$$2E\psi^*\alpha_x\psi = c\{\psi^*\alpha_x\underline{\alpha}\cdot\underline{p}\,\psi + p^*\psi^*\cdot\alpha\,\alpha_x\psi\} - mc^2\psi^*\psi(\alpha_x\beta + \ldots)$$

$= 0$

$$= c\left[\psi^* p_x\psi + p_x^*\psi^*\psi + \psi^*\alpha_x\alpha_y p_y\psi - p_y^*\psi^*\alpha_y\alpha_x\psi\right.$$

etc.

Lec. 19

$$p_y = -i\hbar\frac{\partial}{\partial y}$$

$$\therefore \frac{2E}{c}\psi^*\alpha_x\psi = -i\hbar\left[\psi^*\frac{\partial\psi}{\partial x} - \frac{\partial\psi^*}{\partial x}\psi + \psi^*\alpha_x\alpha_y\frac{\partial\psi}{\partial y} + \frac{\partial\psi^*}{\partial y}\alpha_x\alpha_y\psi\right.$$

etc. —

$\alpha_x\alpha_y = i\sigma_z$

$$= -i\hbar\left[\psi^*\frac{\partial\psi}{\partial x} - \frac{\partial\psi^*}{\partial x}\psi\right] + \hbar\frac{\partial}{\partial y}(\psi^*\sigma_z\psi) - \hbar\frac{\partial}{\partial z}(\psi^*\sigma_y\psi)$$

$$\therefore \psi^*\underline{\alpha}\cdot\psi = -\frac{i\hbar c}{2E}(\psi^*\operatorname{grad}\psi - \psi\operatorname{grad}\psi^*) + \frac{\hbar c}{2E}\nabla\times(\psi^*\underline{\sigma}\cdot\psi)$$

σ is connected with magnetic moment.

Integrate over all space; if ψ vanishes well enough at ∞

(∫ curl vanishes).

$$\int\psi^*\underline{\alpha}\,\psi = -\frac{i\hbar c}{E}\int\psi^*\operatorname{grad}\psi$$

$$= \frac{c}{E}\int\psi^* p\,\psi$$

i.e. $\left(\frac{v}{c}\right) = \frac{c}{E}(p)$ (classical relativistic relation between v & p diagonal elements matrices)

$\underline{\sigma}$-term: Schrödinger's Zitterbewegung

Angular Momentum

Classically: $M_3 = x p_y - y p_x$

$$\dot{M}_3 = \frac{i}{\hbar}(H M_3 - M_3 H) \qquad H = c\,\underline{\alpha}\cdot\underline{p} - mc^2$$

$$= \frac{ic}{\hbar}\left(\underline{\alpha}\cdot\underline{p}\,M_3 - M_3\,\underline{\alpha}\cdot\underline{p}\right) = \frac{ic}{\hbar}\left(\alpha_x p_x \cdot x p_y - x p_y \alpha_x p_x - \alpha_y p_y\, y p_x + y p_x \alpha_y p_y\right)$$

$$= \frac{ic}{\hbar}\left(\alpha_x p_y(-i\hbar) + \alpha_y p_x(i\hbar)\right) = c(\alpha_x p_y - \alpha_y p_x).$$

or $\quad \dot{\underline{M}} = c\,\underline{\alpha}\times\underline{p}$.

$$\underline{S} = \tfrac{1}{2}\hbar\,\underline{\sigma}$$

$$S_3 = -\tfrac{1}{2}\hbar\, i\,\alpha_x\alpha_y$$

$$\dot{S}_3 = \tfrac{1}{2}\left[H, \alpha_x\alpha_y\right]$$

Now $\alpha_x\alpha_x\alpha_y = -\alpha_x\alpha_y\alpha_x$

$\alpha_y\alpha_x\alpha_y = -\alpha_x\alpha_y\alpha_y$

$\alpha_3\alpha_x\alpha_y = \alpha_x\alpha_y\alpha_3$

$\beta\alpha_x\alpha_y = \alpha_x\alpha_y\beta$

$$\dot{S}_3 = \tfrac{1}{2}c\left[\alpha\cdot p, \alpha_x\alpha_y\right] = \frac{c}{2}\left[p_x\cdot 2\alpha_y + p_y(-2\alpha_x)\right]$$

$$= c\,(p_x\alpha_y - \alpha_x p_y). = -\dot{M}$$

$$\therefore \quad \dot{M} + \dot{S} = 0, \text{ or } \frac{d}{dt}(M+S) = 0$$

$$M + S = \underline{r}\times\underline{p} + \tfrac{1}{2}\hbar\,\underline{\sigma}.$$

Conservation of $(M+S)$, which differs from classical in addition of spin to orbital momentum. usually M, S not constants of motion, only their sum.

σ_3 is diagonal, has eigenvalues ± 1.

if ψ has only ψ_1, ψ_3, then $\sigma_3\psi_{1,3} = \psi_{1,3}$ and

S_3 has value $\hbar/2$. if it has only $\psi_{2,4}$, $\sigma_3\psi_{2,4} = -\psi_{2,4}$

and S_3 has value $-\hbar/2$.

spin arises naturally from Dirac equation — one of the best successes of Dirac theory.

It is postulate: $\psi^+\psi$ positive definite.

∴ Dirac is ...
∴ ... constant, ...
∴ several components of wave fn; then spin arises as part of conserved angular momentum.

In field, Dirac Operator is: $i\hbar\frac{\partial}{\partial t} - V + i\hbar c\, \alpha\cdot(\text{grad} - e\, \alpha\cdot A) + mc^2\beta$

Consider: $\left(i\hbar\frac{\partial}{\partial t} + V + i\hbar c\, \alpha\cdot\text{grad} + e\,\alpha\cdot A + mc^2\beta\right)\psi = 0$

$- \left(i\hbar\frac{\partial}{\partial t} - V\right)^2\psi + (i\hbar c\,\text{grad} - eA)^2\psi + (mc^2)^2\psi$ + other terms.

Terms mixing $\alpha\,\beta$ vanish; so do those with $V, \frac{\partial}{\partial t}$ ... also ... derivatives vanish; and mixed ..., but V, grad don't commute, get terms like $\alpha_x\alpha_y\left(\frac{\partial A_x}{\partial x} - \frac{\partial A_y}{\partial x}\right)$.

← E H

June 6 1941 if $V = V(r)$, $A = 0$, $\underline{r}\times\underline{p} + \frac{1}{2}\hbar\underline{\sigma}$ is constant.

$\frac{dx}{dt} = \alpha_x c$

$\frac{dp_x}{dt} = -\frac{\partial}{\partial x}(V + e\,A\cdot\alpha)$

$E\psi = \alpha\cdot(cp + eA)\psi - mc^2\beta\psi + V\psi$

write conj., multiply ... $\psi\alpha_x$ conj ..., add,

& get $E\psi^*\alpha\psi = -\frac{\hbar c}{2}\psi^*(\text{grad} + eA)\psi - \psi ... + \frac{\hbar c}{2}$ conj

Dirac Equation:

$$\left(\frac{1}{c}\frac{\partial}{\partial t} + \alpha\cdot\left(\text{grad} - \frac{ie}{\hbar c}A\right) + \frac{imc}{\hbar}\beta - \frac{i}{\hbar c}V\right)\psi = 0$$

Operate on this with $\left(-\frac{1}{c}\frac{\partial}{\partial t} + \alpha\cdot\left(\text{grad} - \frac{ie}{\hbar c}A\right) + \frac{imc}{\hbar}\beta + \frac{i}{\hbar c}V\right)$

this gives: $\Big\{ -\left(\frac{1}{c}\frac{\partial}{\partial t} - \frac{i}{\hbar c}V\right)^2 + \left(\text{grad} - \frac{ie}{\hbar c}A\right)^2 - \frac{m^2c^2}{\hbar^2} - \frac{i}{\hbar c}\alpha\cdot\text{grad}\,V$

mixed terms with β alone vanish $\qquad + \frac{ie}{\hbar c}\frac{1}{c}\alpha\cdot\frac{\partial A}{\partial t} - \frac{ie}{\hbar c}(\alpha_x\alpha_y\,\text{curl}_z A + \dots)\Big\}\psi$

" " α, β "

$\alpha_x\alpha_y = i\sigma_z$

$\text{curl}_z A = H_z$

$$-\frac{i}{\hbar c}\alpha\cdot\text{grad}\,V - \frac{ie}{\hbar c}\frac{1}{c}\alpha\cdot\frac{\partial A}{\partial t} = -\frac{ie}{\hbar c}\alpha\cdot\left[\text{grad}\frac{V}{e} + \frac{1}{c}\dot{A}\right]$$

$$= \frac{ie}{\hbar c}\alpha\cdot E \qquad E = -\text{grad}\,\phi - \frac{1}{c}\dot{A}, \quad e\phi = V$$

multiply by $-\hbar^2 c^2$:

$$\left\{\left(i\hbar\frac{\partial}{\partial t} - V\right)^2 - c^2\left(-i\hbar\,\text{grad} - \frac{e}{c}A\right)^2 - (mc^2)^2 - i e\hbar c\,\alpha\cdot E + e\hbar c\,\sigma\cdot H\right\}\psi = 0$$

gives the Dirac eq'n ↗

K–G eq'n: $\left[\left(i\hbar\frac{\partial}{\partial t} - V\right)^2 - c^2\left(-i\hbar\,\text{grad} - eA\right)^2 - (mc^2)^2\right]\psi = 0$

(Classical relativistic energy-momentum relation)

$$\left((E - V)^2 = c^2(p - eA)^2 + m^2c^4\right)$$

Dirac → K-G if no external field

But two new terms in field

In general, if an energy term of the form $\underline{\mu}\cdot\underline{H}$, we call μ the magnetic moment.

If magnetic field small & treat as a perturbation of energy E_0 without H, then choose E so that $(E-V)^2 + \hbar c e \, \sigma\cdot H = (E_0 - V)^2$; then a ψ satisfying K.G eq'n with E_0 satisfies Dirac eq'n with E.

This can be done if $V \ll E$ i.e. $V \ll mc^2$.

then
$$(E-V)^2 - (E_0-V)^2 \simeq E^2 - 2EV - E_0^2 + 2E_0 V$$
$$= (E-E_0)(E+E_0-2V)$$
$$\sim (E-E_0)\,2E_0 .$$

$$\therefore (E-E_0)\,2E_0 \sim -e\hbar c\, \sigma\cdot H .$$

$$E - E_0 \sim -\frac{e\hbar c}{2E_0}\,\sigma\cdot H$$

$\therefore$ magnetic moment associated with spin is
$$\underline{\mu} = -\frac{e\hbar c}{2E_0}\,\underline{\sigma}$$

for non-relativistic case $E_0 \sim mc^2$,
$$\underline{\mu} = -\frac{e\hbar}{2mc}\,\underline{\sigma}$$

σ_3 has eigenvalues $+1, -1$, $\therefore \mu_3$ has eigenvalues $\pm\frac{eh}{2mc}$ (Bohr magneton μ_0)

Ratio of mag. mom. to ang. mom. is $\frac{e\hbar}{2mc} : \frac{\hbar}{2} = \frac{e}{mc}$

this is twice as great as gyromagnetic ratio for orbital motion – $\frac{\text{mag. mom}}{\text{ang. mom}} = \frac{e}{2mc}$ for orbital motion

Anomalous Zeeman effect
Van Vleck "Dispersion & Electric const."

Condon & Shortley
Kemble

Jan 8) 2nd order Dirac eq'n:

$$\left[\left(i\hbar\frac{\partial}{\partial t}-V\right)^2 - c^2\left(-i\hbar\,\text{grad} - \frac{e}{c}\underline{A}\right)^2 - m^2c^4 + e\hbar c\,\underline{\sigma}\cdot\underline{H} - ie\hbar c\,\underline{\alpha}\cdot\underline{E}\right]\psi =$$

The two smaller Dirac f'n's are to larger ones $\sim \sqrt{\frac{E-mc^2}{mc^2}}$

Hence for $E \sim mc^2$, can neglect two small comp's.

write ψ as two row matrix: $\psi = \begin{pmatrix}\varphi \\ \chi\end{pmatrix}$

$\varphi = \begin{pmatrix}\psi_1 \\ \psi_2\end{pmatrix}$ – small comp's.

$\chi = \begin{pmatrix}\psi_3 \\ \psi_4\end{pmatrix}$ – large comp's

Then $\alpha = \begin{pmatrix}0 & \sigma \\ \sigma & 0\end{pmatrix}$ $\quad \underline{\sigma} = \begin{pmatrix}k & i-ij \\ i+ij & -k\end{pmatrix}$

$\beta = \begin{pmatrix}1 & 0 \\ 0 & -1\end{pmatrix}$

Then Dirac eq'n becomes:

$$(E-V)\psi = \alpha\cdot(cp-eA)\psi - \beta mc^2\psi$$

$$\therefore \quad (E-V)\varphi = \sigma\cdot(cp-eA)\chi - mc^2\varphi$$

$$(E-V)\chi = \sigma\cdot(cp-eA)\varphi + mc^2\chi$$

or : $\begin{cases}(E+mc^2-V)\,\varphi = \sigma\cdot(cp-eA)\,\chi \\ (E-mc^2-V)\,\chi = \sigma\cdot(cp-eA)\,\varphi\end{cases}$

if $E \sim mc^2$:

V small: $(2mc^2 \cancel{-V})\,\varphi = \sigma\cdot(-i\hbar c\,\text{grad} - eA)\,\chi$

$$\varphi = -\sigma\cdot(i\hbar\,\text{grad} + eA)\frac{\chi}{2mc^2}$$

∴ 2nd order eq'n gives:

$$\left((E-V)^2 - c^2(\hbar\,\text{grad} + \tfrac{e}{c}A)^2 - m^2c^4 + e\hbar c\,\underline{\sigma}\cdot\underline{H}\right)\chi = ie\hbar c\,\alpha\cdot E\,\chi$$

$$= ie\hbar c\;E\cdot\sigma\,\varphi$$

$$= ie\hbar c\;E\cdot\frac{\sigma(-\sigma\cdot(c\hbar\,\text{grad}+eA)\chi}{2mc^2}$$

neglecting A : $$= +\frac{e\hbar^2}{2m}\,E\cdot\sigma\;\sigma\cdot\text{grad}\,\chi$$

can show that:

$$(E\cdot\sigma\;\underline{\sigma}\cdot\text{grad}\,\chi) = \underline{E}\cdot\text{grad}\,\chi + i(\sigma\times E)\cdot\text{grad}\,\chi$$

$$= E\cdot\text{grad}\,\chi + i\,\underline{\sigma}\cdot(\underline{E}\times\text{grad}\,\chi)$$

if central field, $\varphi = \varphi(r)$,

$$\underline{E} = -\frac{\partial\varphi}{\partial r}\,\frac{\underline{r}}{r}.$$

and 2nd term above is

$$\frac{1}{r}\frac{\partial\varphi}{\partial r}\,\sigma\cdot\underline{r}\times\text{grad}\,\chi$$

But orbital mom. $= \underline{r}\times\underline{p} = \underline{r}\times\hbar\,\text{grad}$

∴ $\underline{\sigma}\cdot\underline{r}\times\text{grad}\,\chi$ is spin-orbit interaction

$$\frac{1}{r}\frac{\partial\varphi}{\partial r}\,\underline{\sigma}\cdot\underline{M}\,\chi$$

In nuclei, forces are non electric mostly, - electric & magnetic effects are small. But still get this spin orbit interaction because of Thomas effect - due to accel. of particle - effect is negative of that for the case when field is present. (Inglis)

[But apparently not sufficient to cause splitting of ground state of He^5].

$$\therefore \left((E-V)^2 + c^2(\hbar\,\text{grad} - i\tfrac{e}{c}A)^2 - m^2c^4 + e\hbar c\,\underline{\sigma}\cdot\underline{H} - \frac{e\hbar^2}{2m}(E + i(\sigma\times E))\cdot\text{grad}\right)\chi = 0$$

for central field $E = -\frac{1}{r}\frac{\partial\varphi}{\partial r}\underline{r}$

$$E\cdot\text{grad}\,\chi = -\frac{1}{r}\frac{\partial\varphi}{\partial r}\underline{r}\cdot\text{grad}\,\chi$$

$$= -\frac{\partial\varphi}{\partial r}\frac{\partial\chi}{\partial r}.$$

$$\therefore \left[(E-V)^2 + c^2(\hbar\,\text{grad} - \tfrac{ie}{c}A)^2 - m^2c^4 + e\hbar c\,\underline{\sigma}\cdot\underline{H} - \frac{dV}{dr}\left(-\frac{\hbar^2}{m}\frac{\partial}{\partial r} + \frac{\hbar}{2m}\frac{1}{r}\sigma\cdot M\right)\right]\chi$$

if $E = mc^2 + W$

$$(E-V)^2 - m^2c^4 = (W - V + mc^2)^2 - m^2c^4$$

$$= (W-V)^2 + 2mc^2(W-V).$$

↳ small relativistic perturbation

$$\therefore \left[W - V + \frac{\hbar^2}{2m}(\text{grad} - i\frac{e}{\hbar c}A)^2 + \frac{(W-V)^2}{2mc^2} + \frac{e\hbar}{mc}\underline{\sigma}\cdot\underline{H} - \left(\frac{\hbar}{mc}\right)^2\frac{dV}{dr}\left(-\frac{\partial}{\partial r} + \frac{\sigma\cdot M}{2\hbar r}\right)\right]$$

1st 3 terms give Schroedinger eq'n; remaining terms are small perturbations.

~~$1/\nu$ terms — A·grad~~
(small)

$$\left(W - V + \frac{\hbar^2}{2m}\nabla^2\right)\chi = \frac{ie\hbar}{mc} A \cdot \text{grad}\,\chi$$ Interaction of ext. mag. field w arbitr mom - Zeeman-effect. paramagnetism

$$+ \frac{e^2}{2mc^2} A^2 \chi$$ Important if no magnetic moment - gives rise to diamagnetism (Van Vleck)

$$-\frac{(W-V)^2}{2mc^2}\chi$$ - ordinary relativistic correction. (without spin) always lowers eigenvalues

Pauli - (pre Dirac) explains fine structure (except →)

$$-\frac{e\hbar}{2mc} H \cdot \sigma \chi$$ spin - external mag. field interaction

$$+\left(\frac{\hbar}{2mc}\right)^2 \frac{\partial V}{\partial r}\frac{\partial \chi}{\partial r}$$ gives interaction only for s electrons. replaces ordinary spin-orbit there.

$$+\left(\frac{\hbar}{2mc}\right)^2 \frac{1}{\hbar}\frac{\sigma \cdot M}{r}\chi$$ spin-orbit interaction.

$L = \frac{M}{\hbar}$ $$= \left(\frac{\hbar}{2mc}\right)^2 \frac{\partial V}{\partial r}\frac{\sigma \cdot L}{r}\chi$$

9/41

$$\chi = \chi(r)\begin{pmatrix} Y_l^{m-1/2} \\ Y_l^{m+1/2} \end{pmatrix}.$$

Pauli, Zeit. für Phys. 43 ..
Bethe, Handbuch 24₁, 30?

For states of total ang mom j,

$$2L \cdot S = j(j+1) - l(l+1) - s(s+1);$$

$$s = 1/2, \quad j = l \pm 1/2,$$

$$2L \cdot S = \begin{cases} l \\ -(l+1) \end{cases}$$

Coulomb field $\quad V = -\frac{e^2}{r}$

$$\frac{1}{r}\frac{\partial V}{\partial r} = \frac{e^2}{r^3}$$

$\therefore$ 1st order correction is: $\left(\frac{\hbar}{mc}\right)^2 \frac{e^2}{2} \begin{pmatrix} l \\ -(l+1) \end{pmatrix} \overline{r^{-3}}$

$$\overline{r^{-3}} = \frac{1}{n^3 (l+1)(l+\frac{1}{2}) l \;\; a_0^3} \qquad a_0 = \text{Bohr radius}$$

if $l = 0$, $\; j = \frac{1}{2}$, $s = \frac{1}{2}$, $\; L \cdot S = 0$

and $\overline{r^{-3}}$ diverges for s-states.

$\therefore$ for $l = 0$ correction is indeterminate.

$\therefore$ go back to derivation; instead of $(2mc)^2$ in denominator, should have: $\left(2mc - \frac{V}{c}\right)^2$ but $-V \sim \frac{1}{r}$ $\therefore$ for small r integral is actually $\frac{r^{-3}}{(r^{-1})^2} = r^{-1}$ & converges even for s-states.

$\therefore$ spin-orbit interaction is zero, in contradiction to experiment. other term: $\left(\frac{\hbar}{mc}\right)^2 \frac{dV}{\partial r}\frac{\partial \chi}{\partial r}$

gives: $\int \frac{e^2}{r^2} \chi \frac{\partial \chi}{\partial r} 4\pi r^2 dr = \frac{1}{2}\chi^2 \Big|_0^\infty$

which gives contribution only for s-states – (only s states are not zero at origin). turns out that this gives same result as if l's were cancelled above.

(This result only for Coulomb field)

$j = l + \frac{1}{2}$ is raised, $l - \frac{1}{2}$ is lowered by spin-orbit interaction

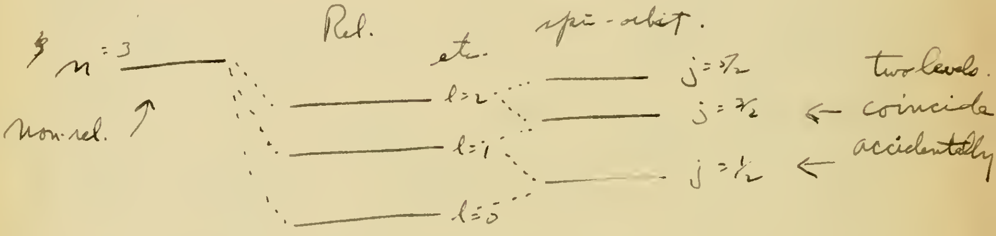
~~Relativistic~~ correction $-\frac{(W-V)^2}{mc^2} = \frac{(W+\frac{e^2}{r})^2}{mc^2}$ greater correction

for wave functions concentrated near origin – i.e. for small l.

Whole variation : relativistic $-\frac{1}{2}\alpha^2 \frac{R_y}{n^3}\left(\frac{1}{l+\frac{1}{2}} - \frac{3}{4n}\right)$ $\alpha = \frac{e^2}{\hbar c} = \frac{1}{137}$

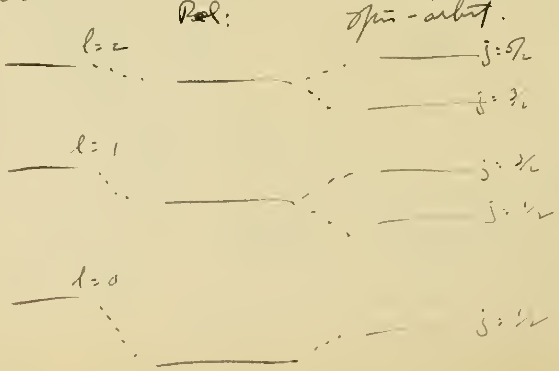
$\sim \frac{1}{20{,}000}$ of freq. of H lines.

spin-orbit interaction : $\frac{1}{4}\alpha^2 \frac{R_y}{(l+\frac{1}{2})n^3}\begin{pmatrix}\frac{1}{l+1} \\ -\frac{1}{l}\end{pmatrix}$



Hydrogen

But in Alkali l-levels are already separated non-relativistically



With nucleus Z, dimensions of wave f'ns are reduced in the ratio Z; ∴ $\overline{r^{-3}}$ is multiplied by Z^3, V & $\frac{\partial V}{\partial r}$ by Z; and rel. & sp-orbit interactions are all multiplied by Z^4.

∴ fine structure becomes much larger –

In X-ray spectra, inner electrons move almost in Coulomb fields, ∴ almost the same fine structure as H, only introducing small ~~screening~~ "constants" – $Z-s$ effective nuclear charge –

But relativistic effect much larger –

Sommerfeld

Pauli theory can't calculate energies to order α^4

— $d_{5/2}$
— $d_{3/2}$
"relativistic doublet" { — $p_{3/2}$, — $p_{1/2}$ }
"screening doublet" { — $p_{1/2}$, — $s_{1/2}$ }

Can get wave functions to order α^2 – useful for intensities of alkali spectra.

Doublet lines should have intensity ratio 2:1 for p – s transitions. (statist. wt. for $j = 3/2 = 2j+1 = 4$, $j = 1/2$, $2j+1 = 2$) this is well followed in Na, K, fairly well in Rb not well in Cs; necessary to use relativistic wave f'ns instead of 1st order –

Fermi Zeitz. f. Phys. 1932 ? ?

Direct solution of Dirac eq'n's for central field.

Dirac - Proc. Roy. Soc.
also by Gordon, & Darwin

get the old Sommerfeld levels -
" fine structure formula

[Jun 11'41] An atom lacking one atom of a complete shell has same energy levels as one with one atom in filled shell, considering electrostatic interaction. But spin-orbit interaction inverts doublets. In general, "inverted multiplets" when state of highest j lies lowest.

Levels of a multiplet are $A + 2B\underline{L}\cdot\underline{S} = A + B(j(j+1) - l(l+1) - s(s+1))$

and $E_j - E_{j-1} = 2BJ$ Landé interval rule -

e.g. ^4D: $7/2$ — ↕ 7, $5/2$ — ↕ 5, $3/2$ — ↕ 3, $J = 1/2$; $l = 2$, $S = 3/2$

But interval rule breaks down in He, Li^+ because field deviates strongly from central field

Heisenberg first not quite correctly, then Breit correctly calculated fine structure for 2^3P, eg: — J = 0, = J = 1, J = 2. Inverted multiplet, no interval rule; ratio 7:1 instead of 2:

magnetic interaction between spins of two electrons forms: — $l-1$, - - - $l+1$ - -, — l

$\left(\frac{s_1 \cdot r\, s_2 \cdot r}{r^2} - \frac{1}{3} s_1 \cdot s_2\right)$ which always gives a splitting:

then also ordinary spin-orbit: — $l+1$, — l, — $l-1$ actual levels are combination of both

Alkali abnormalities: d states of Rb are inverted due to exchange between d electron + some s electrons.

Negative energy levels. Free electron: $E = \pm c\sqrt{p^2 + m^2c^2}$

(classically can forget negative energies, since if energy is initially +, it remains + forever). Q.M.: $E\psi = c\,\underline{\alpha}\cdot\underline{p}\,\psi - \beta mc^2\psi$

$$\frac{E}{c}\psi_1 = p_x\psi_4 - ip_y\psi_4 + p_3\psi_3 - mc\,\psi_4$$
$$\psi_2 = (p_x + ip_y)\psi_3 \quad p_3\psi_4 - mc\,\psi_2$$
$$\psi_3 = (p_x - ip_y)\psi_2 - p_3\psi_1 + mc\,\psi_3$$

If $\psi_4 = 0$: $\quad \left(\frac{E+mc^2}{c}\right)\psi_1 = p_3 \psi_3$

$$\therefore \quad \psi_2 = (p_x + ip_y)\psi_3$$

$$\frac{E-mc^2}{c}\psi_3 = (p_x - ip_y)\psi_2 + p_3\psi_1$$

$$\left(\frac{E+mc^2}{c}\right)\left(\frac{E-mc^2}{c}\right)\psi_3 = \left[(p_x - ip_y)(p_x+ip_y) + p_3 p_3\right]\psi_3$$

$$\therefore \quad E^2 - m^2c^4 = c^2p^2$$ — so this is a sol'n

$$1 = \sum_{i=1}^{3}|\psi_i|^2 = |\psi_3|^2 \frac{c^2p^2}{(E+mc^2)^2} + 1 = |\psi_3|^2\left[\frac{c^2p^2+(E+mc^2)^2}{(E+mc^2)^2}\right] \cong \frac{2E}{E+mc^2}$$

$$\therefore \quad \psi_3 = \sqrt{\frac{E+mc^2}{2E}}.$$

sol'ns:
$$\frac{1}{\sqrt{2E(E+mc^2)}}\begin{pmatrix} cp_3 \\ c(p_x+ip_3) \\ E+mc^2 \\ 0 \end{pmatrix} \qquad \frac{1}{\sqrt{\ }}\begin{pmatrix} c(p_x-ip_y) \\ -cp_3 \\ 0 \\ E+mc^2 \end{pmatrix}$$

$$\frac{1}{\sqrt{2E(E-mc^2)}}\begin{pmatrix} cp_3 \\ c(p_x+ip_y) \\ -E+mc^2 \\ 0 \end{pmatrix} \qquad \frac{1}{\sqrt{\ }}\begin{pmatrix} c(p_x-ip_y) \\ -cp_3 \\ 0 \\ -E+mc^2 \end{pmatrix}$$

positive E: ψ_3, ψ_4 large $\qquad \sum_K \psi_K^* \psi_K' = 0$

negative E: $\psi_1 \; \psi_2$ large

Dirac assumed all negative energy states filled by Pauli principle; (Fermi statistics necessary therefore). + positive energy electrons affect act as they should; + must go to negative states; but the reverse may happen; electron in negative state may absorb photon + go to pos. state, leaving a hole which acts like a positive charge. Dirac at first thought it was proton; but Oppenheimer showed it must act just like electron except for charge. Anderson in 1933 observed positrons; Blackett + others observed "pair formation" by Th C'' γ-rays (2.62 Mev) in cosmic rays + measured mass from: $W_+ + W_- = h\nu - 2mc^2$ + it was right

Jan 14 '41 Radiation Theory: Expand potentials in Fourier series in big box of dimension $\Omega = L^3$

Then $\underline{A} = \sum_{\underline{k}} \underline{a}_{\underline{k}} \exp(i\underline{k}\cdot\underline{r})$ $k_x = \frac{2\pi}{L}\kappa_x$ κ_x an integer (similarly y

since A is real, $\underline{a}_{\underline{k}} = \underline{a}^*_{-k}$

No of normal modes $= \left(\frac{L}{2\pi}\right)^3 dk_x\, dk_y\, dk_z = \frac{\Omega}{(2\pi)^3} d\underline{k}$.

In absence of charges + currents, $\Box^2 \underline{A} = 0$;

$$+\frac{1}{c^2}\frac{\partial^2 a_k}{\partial t^2} = -k^2 a_k$$

I field free case:

$$\mathcal{H} = \frac{1}{8\pi}\int (E^2 + H^2)\, d\tau$$

$$\therefore a_k \sim e^{\pm i\omega t} \qquad \omega = ck.$$

Heisenberg + Pauli considered field variables at each point; one gets commutation relations like $[E(r), H(r')] \sim \delta(r - r')$; gets quite complicated –

Dirac (+ later Fermi) – Fourier expansion – this theory can do all that H-P theory does, only more simply –

Expand: $\varphi = \sum \varphi_k e^{i\underline{k}\cdot\underline{r}}$, $H = \text{curl} A = \sum i\,\underline{k}\times\underline{a}\, e^{i\underline{k}\cdot\underline{r}} = \sum -i\underline{k}\times$

$$E = -\nabla\varphi + \frac{1}{c}\dot{\underline{A}}) = -\sum\left(\frac{1}{c}\dot{a}_k + i\underline{k}\,\varphi_k\right)e^{i}$$

Then $H^2 = \sum_k \sum_{l'} i(\underline{k}\times\underline{a}_k)e^{i\underline{k}\cdot\underline{r}}[-i(l'\times a^*_{l'})]e^{-il'\cdot r}$

$$= \sum_k \sum_{k'} (k\times a_k)(k'\times a^*_{k'})e^{i(\underline{k}-\underline{k}')\cdot r}$$

$$E^2 = \sum_{k,k'}\left[\frac{1}{c^2}\dot{a}_k\dot{a}^*_{k'} + k\cdot k'\varphi_k\varphi^*_{k'} - \frac{i}{c}\left(\dot{a}_k\cdot \underline{k}'\varphi^*_{k'} - \dot{a}^*_{k'}\cdot\underline{k}\,\varphi_k\right)\right]e^{i(k}$$

Integrate over box $L^3 = \Omega$ all integrals with $k \neq k'$ will $= 0$, if $k = k'$ get volume of

$$\therefore \frac{1}{8\pi}\int (E^2 + H^2)\, d\tau = \frac{\Omega}{8\pi}\sum_k |k\times a_k|^2 + k^2|\varphi_k|^2 + \frac{|\dot{a}|^2}{c^2} + \frac{i}{c}(\dot{\varphi}_k\varphi^*_k - \dot{\varphi}^*$$

Note that $\text{div} A = \sum i k\cdot a_k e^{i(k\cdot r)}$

and $\text{div} A = -\frac{1}{c}\dot{\varphi}$]

$\therefore \text{div} A = -\frac{1}{c}\sum \dot{\varphi}_k e^{ik\cdot r}$

$\therefore -\frac{1}{c}\dot{\varphi}_k = i k\cdot a_k$

[illegible]

introduce polarization [illegible]

[illegible]

m (641)

$\frac{\Omega}{(2\pi)^3}\, d\underline{k}$ normal modes ;

$\mathcal{H} = \frac{\Omega}{8\pi} \sum k^2 a_k^2 + \frac{1}{c^2} \dot{a}_k^2$

$b_k = \sqrt{\frac{\Omega}{4\pi}}\, \frac{a_k}{c}$

then $\mathcal{H} = \frac{1}{2} \sum \omega_k^2 a_k^2 + p_k^2 \qquad \omega_k = ck$.

$p_k = \dot{b}_k$

(really $\dot{b} = \frac{\partial \mathcal{H}}{\partial p_k} = p_k^*$

$\underline{A} = c\sqrt{\frac{4\pi}{\Omega}} \sum_k b_k e^{i\underline{k}\cdot\underline{r}}$

treat b's as coord's, p's as momenta .

Hamiltonian is separable .

then solution $\Phi = \prod_k \varphi(b_k)$.

Each φ satisfies : $\frac{\hbar^2}{2} \frac{\partial^2 \varphi_k}{\partial b_k^2} + (E - \frac{1}{2}\omega_k^2 b_k^2)\varphi = 0$

Where $\varphi = H_{n_k}(b_k) \quad E_k = (n_k + \frac{1}{2})\hbar\omega_k$

$\therefore E = \sum E_k = \sum_k \hbar\omega_k (n_k + \frac{1}{2})$.

If all n's are zero, no radiation $E = \frac{1}{2}\sum \hbar\omega_k$ which is infinite .

I infinite ... for energy ... exponent + ... the only energy changes. But in relativity any energy has gravitational action this again not so serious, since resultant force would be zero, since the energy density is the same everywhere. Anyhow it can be eliminated by using something like $(E+iH)\cdot(E-iH)$ instead of E^2+H^2 for Hamiltonian.

Serious difficulties in connection with self-energies — infinite energy ...

If we have j particles: (electrons)

$$\mathcal{H} = \underbrace{\sum_j c\,\alpha_j\cdot p_j - mc^2\beta_j + V(r_j)}_{\text{electron}} + \underbrace{\tfrac{1}{2}\sum_k(\omega_k^2 b_k^2 + p_k^2)}_{\text{radiation}} - \underbrace{\sum_j e\,\alpha_j\cdot A(r_j)}_{\text{interaction}}$$

α_j, β_j, r_j are Dirac ... + position of j'th electron.

But $A = c\sqrt{\frac{4\pi}{\Omega}}\sum_k b_k e^{ik\cdot r}$

$\therefore$ Interaction is: $-ec\sqrt{\frac{4\pi}{\Omega}}\sum_j \alpha_j\cdot\sum_k b_k e^{ik\cdot r_j}$

(b's commute with all ... concerning electron)

Wave fn will be $F(r_j, b_k)$

Without interaction $F = \Psi(r_j)\,\Phi(b_k)$.

M: state of electrons

n_k: state of field oscillators

In general Ψ not separable because of elect. inter. of electrons

Transition probabilities for small times are: $\int F^*_{\text{final}}\,(\text{interaction})\,F_{\text{initial}}\,d\tau_M\,db_k$

(b_k in 1st approx.)

Since F contains $\prod_k \phi_{n_k}(b_k)$, we must have $n_{k'}^{\text{final}} = n_{k'}^{\text{initial}}$ $\quad k'\neq k$

$n_k^{\text{final}} = n_k^{\text{initial}} \pm 1 \quad k' = k$.

i.e. to get a transition one n_k changes by one unit. then $\int b_k \phi_{\text{fin}}\phi_{\text{initial}}\,db = \sqrt{\frac{1}{2}\frac{\hbar}{\omega_k}n_k}$

$\therefore (\cdots n_k \cdots|\text{int}|\cdots n_k-1\cdots) = -ec\sqrt{\frac{4\pi}{\Omega}}\cdot\sqrt{\frac{1}{2}\frac{\hbar}{\omega_k}n_k}\cdot\sum_j \alpha_{j\,pol.}\,e^{ik\cdot r_j}$

$(\cdots n_k \cdots|\text{int}|\cdots n_k+1\cdots) = \;-\;-\;-\;(n_k+1)$

$\alpha_{j\,pol}$ is comp. of α_j in direction of $\frac{k}{...}$ ... $\alpha_j\cdot u_k$

Complete matrix element: $\sum_j\int\Psi^*_{\text{final}}\,\alpha_j\cdot u_k\,e^{ik\cdot r_j}\,\Psi_{\text{initial}}\,d\tau_M$ Without exponential, this is just the sum of the currents of all electrons. Retardation factor $e^{ik\cdot r_j}$.

Dipole radiation: $\int\psi_f^*\sum_j\alpha_j\,\psi_i\,d\tau = \frac{i}{\hbar c}(E_f - E_i)\int\psi_f^*\sum_j x_j\,\psi_i$ since α is ... with the derivative

Read Heitler → ...

In calculating matrix elements expand $e^{i\mathbf{k}\cdot\mathbf{r}}$ not in power series, but in spherical harmonics: $e^{i\mathbf{k}\cdot\mathbf{r}_j} = \frac{1}{\sqrt{r}} \sum i^l J_{l+\frac{1}{2}}(kr) P_l(\theta)$

l^{th} term gives rise to { electric 2^{l+1}-pole, magnetic 2^l-pole } (see Heitler's paper)

(this arises from combinations of transformation properties of α + spherical harmonics)

electric 2^{l+1}-pole from $l, l+2$ ($J_{l+\frac{1}{2}}$, $J_{l+\frac{5}{2}}$); magnetic 2^l-pole from l: $J_{l+\frac{1}{2}}$

$kr \ll 1$: $\frac{J_{l+\frac{1}{2}}}{\sqrt{r}} \sim (kr)^l$.

Dipole: $\frac{E_i - E_f}{i\hbar}\int \psi_f^* x\, \psi_i$ this also from elementary theory. Selection rules: l can change by one unit; also 1-unit change in field oscillators.

electric 2^{l+1}-pole: $|\Delta J| \leq l+1$ parity multiplied by $(-1)^{l+1}$

magnetic 2^l-pole $\Delta J \leq l$ . . . .

Non-relativistic q.m.: α replaced by $\left(\frac{\hbar}{imc}\,\text{grad}\right)$ (velocity = $\frac{\text{momentum}}{m}$).

Radiation processes: classified according to no. of quanta involved.

One quantum: absorption + emission; perturbation theory gives probability per unit time of: $\frac{2\pi}{\hbar}|\text{Matrix el.}|^2 \cdot$ No. of final states per unit energy.

Emission: No. of final states: $\frac{\Omega}{(2\pi)^3} d\mathbf{k} = \frac{\Omega}{8\pi^3} 4\pi k^2 \frac{dk}{dE} = \frac{\Omega}{8\pi^3}\frac{4\pi k^2}{\hbar c}$.

but two directions of polarization ($\therefore \times 2$) but m. selection rule determines polarization vector for a given transition – this must also be considered.

$\therefore$ trans. prob. $\sim k^2 |\text{matrix el.}|^2 \sim \omega^2 \cdot \frac{1}{\omega}|\text{current}|^2 = \omega|\text{current}|^2$ (Ω cancels out as it must)

$\sim \omega^3 |\text{dipole mom.}|^2$

Intensity = $\hbar\omega$ emiss. prob. $\sim \omega^4$.

Absorption: Final state of material system in continuum. Assume $n \neq 0$ for one + only one rad. oscillator. [No. of final states of material system/energy] $\cdot \frac{1}{\omega}\cdot\frac{n}{\Omega}|\text{current}|^2 \sim$ abs. prob. Introduce Rad. density = $\frac{n\hbar\omega}{\Omega}$

then prob. $\sim \frac{\rho}{\omega^2}|\text{current}|^2$(No. fin. states) $\sim \rho|\text{dipole}|^2 N(E)$. $[\rho \sim \frac{1}{\lambda^3} \sim \omega^3]$.

(Einstein derived relation betw. absorption + emission on statistical basis)

Em. = induced emiss.; total emiss. - induced + spontaneous

time of state discrete: simple to calculate only if there is a continuous distribution of radiation energies – can use no. of quanta present/unit energy – i.e. assume an average no. for states in region; ~~total absorption~~ otherwise must know the widths of levels involved. Then abs. prob. $\sim \frac{c}{(\omega-\omega_0)^2 + \frac{1}{2}\gamma^2}$ γ: natural width: i.e. of the 2 states of material system

Emission, really has this shape too]. Weisskopf + Wigner 1932 ~ Z. f. Ph.

Jan 21 '41 E_1: electron energy before $\quad E_1 = E_2 + \nu$ — light emitted.

E_2: " " after: $\quad \underline{p}_1 = \underline{p}_2 + \frac{\underline{\nu}}{c}$, or $\underline{\nu} = c(\underline{p}_1 - \underline{p}_2)$

$\nu^2 = c^2(\underline{p}_1 - \underline{p}_2)^2 = (E_1 - E_2)^2$

$\therefore (E_1 - E_2)^2 - c^2(p_1 - p_2)^2 = 2c^2 p_1 p_2 (1-\cos\theta)$

$\therefore c^2(p_1 - p_2)^2 + 2c^2 p_1 p_2 (1-\cos\theta) = (E_1 - E_2)^2$

$E_1^2 - c^2 p_1^2 + E_2^2 - c^2 p^2 - 2E_1E_2 + 2c^2 p_1 p_2 = 2c^2 p_1 p_2 (1-\cos\theta)$ (with $E_1^2 - c^2p_1^2 = m^2c^4$, $E_2^2 - c^2p^2 = m^2c^4$)

Lorentz transformation to make $p_2 = 0$:

then $c^2 p_1^2 = (E_1 - E_2)^2$

$E_1^2 - m^2c^4 = (E_1 - E_2)^2$

$(E_1 + mc^2)(E_1 - mc^2) = (E_1 \pm mc)^2$.

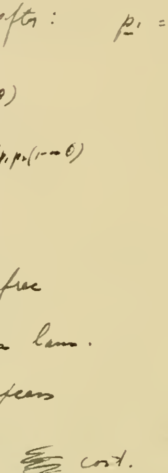
$(E_1 - mc^2) \cdot 2mc^2$ —

or $(E_1 + mc^2) \cdot 2mc^2$

Can calculate eigenfn's.

No (absorption) emission of one quantum by free electron – can't satisfy conservation laws. must have nucleus to take up excess momentum –

In a field of force:



Possible transitions:

1) Discrete - discrete: $\Delta E \ll mc^2$ probability
neglect relativity – use Sch. or Pauli f'ns. constitute matrix elements for transition

dimension of system / wave length of light $\sim \frac{\lambda_c}{\lambda_l} \sim \frac{\hbar/\sqrt{mW}}{ch/W} \sim \sqrt{\frac{W}{mc^2}} < 1$ $\therefore$ retardation negligible. $(e^{ik\cdot r})$ $\therefore$ use

---

2) Continuous – discrete: ~~absorption~~ emission: called recombination (ions absorb el.'s + become stable) (rare) $\sigma \sim 10^{-20}$ cm. (scattering $\sim 10^{-16}$).

absorption: photo-electric effect. $\sim Z^4 \nu^{-3}$
(bigger for more strongly bound atoms) ~~[illegible]~~ also decreases with ν because upper state becomes more nearly free electron state –
angular distribution: $\sim \sin^2\theta$ for low energies – (s shells) p, d shells: $(a + \sin^2\theta)$
high energies: $\sin^2\theta(1 + \alpha \frac{v}{c}\cos\theta)$: higher energy – more run in forward direction

actually photoelectric effect dominates ν^{-3} up to ~ E_B [illegible]
$\nu^{-3.5}$ $\sigma \sim$ [illegible] $< h\nu < mc^2$
ν^{-1} $mc^2 < h\nu$

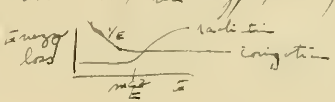
3. continuous - continuum.   quite rare in laboratory experience

[illegible] field. (continuous x-rays).   electron loses energy mostly by producing ions, some by this process.

ordinary x-ray tubes: 10–100 kev. fraction of energy going into x-rays $\sim \frac{E}{\epsilon}$ (E = electron energy) $\epsilon \sim \frac{10^8 \text{ ev}}{Z}$.

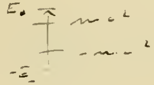
∴ 100 k.v. electron use about 1% of the energy producing x-rays in heaviest element

(higher energies give better yields).



In Stars, very important –

Jan 23 '41 hole left in negative energy states when one electron is removed, acts just like positive electron, with − Energy of hole − p momentum etc.



Pair production $h\nu = E_- + E_+$

$p_\nu \neq p_- + p_+$ (some momentum to atom)

Probability should be in principle, calculated from matrix elements; but complexity of wave functions make it hard. Some approximate (numerical) calculations – Hulme + Jaeger $Z = 82$ [illegible]

Some approximation by: $\psi = \psi_{free}$ + perturbation – use Born approx. $\sim e^2 Z$

(2nd order [illegible] – used to calculate matrix element;

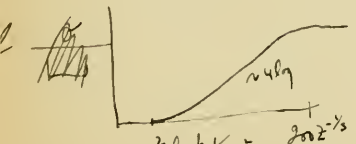
Radiated:

e: interaction between elect. + field   ∴ $\sigma \sim e^6 Z^2$;

$e^2 Z$: " " " + atom.   to have dim. cm², we must have:

$$\sigma \sim \frac{e^2}{\hbar c} Z^2 \left(\frac{e^2}{mc^2}\right)^2 f\left(\frac{h\nu}{mc^2}\right)$$

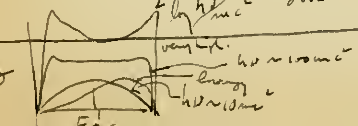
Turns out that $f\left(\frac{h\nu}{mc^2}\right) \sim 1$ for $\frac{h\nu}{mc^2} \sim 1$.



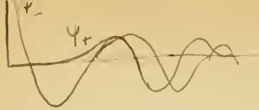
Bethe + Heitler P.R.S. 1934

Main contribution comes from region $\frac{\hbar}{mc} < r < \frac{\hbar}{mc}\frac{h\nu}{mc^2}$.

(radius of atom $= a_0 Z^{-1/3} = \frac{\hbar}{mc} \cdot 137 Z^{-1/3}$.)



This doesn't take into account coulomb repulsion of positron + attraction of electron by nucleus



low energy positrons hard to create
Heitler & Jaeger results good.

γ-Th-C" – $h\nu = 2.6$ Mev Blackett etc. $h\nu \sim 100$ Mev. (cosmic rays) Rossi & Janossi 20% diff which is pretty satisfactory

Emission: Annihilation of pair & emission of quantum. Only possible if a negative energy state empty. Not too likely —

Two quantum processes. (Bethe thinks Heitler's classification poor) (Pair creation really 1st order).

Simultaneous absorption of two (emission/absorption) (unify ?)
emission ⟶ important for radiation between states of zero angular momentum. (impossible, one quantum)
Scattering (one in, one out).

— most important. one gets expressions like these: $\sum_{\text{inter.}} \frac{H_{\text{in, inter.}} H_{\text{inter. fin.}}}{E_{\text{init}} - E_{\text{inter}}}$.

If $h\nu << mc^2$, take H: dipole interaction. neglect other interactions $(e^{ik\cdot r} = 1)$ and $\lambda \to x$.

Thus one gets the dispersion formula: (Kramers & Heisenberg, before Q.M.).

$$\text{Scatt ampl.}_{mn} \sim \sum_k \frac{\lambda_{nk}^{\text{inc.}} \lambda_{km}^{\text{scat.}}}{E_n + \hbar\omega_{\text{inc.}} - E_k} + \frac{\cdots}{E_n - \hbar\omega_{\text{scatt.}} - E_k}$$

$h\nu >>$ binding energies. If only positive E_k are intermediate states considered, Sc. amp. very small. But states $E_k = -mc^2$ give large amplitude about like classical amp. $\sim \frac{e^2}{mc^2}$ (Dirac theory)

Schroedinger theory: A^2 gives main contribution to scattering for large $h\nu$.

X-ray scattering – one gets form factors $\int \rho(r) e^{i(k-k')\cdot r}$

& also gives incoherent scattering (Raman, Compton). $\int \psi_n \psi_m \sum_j e^{i(k-k')\cdot r_j}$

Jan 25, '40 | Compton effect. $E = 2h\nu(1-\cos\theta)\frac{h\nu}{mc^2}$ if $h\nu << mc^2$,
$\Delta\lambda = 2\frac{h}{mc}(1-\cos\theta)$ $\lambda_{\text{inc.}} = \frac{c}{\nu} << \frac{h}{mc}$

and $\nu_{\text{scatt}} << \nu_{\text{incident}}$.

For very high energy γ-rays, electron receives almost all of energy, scattered γ-rays energy negligible.

similar expression to dispersion: $\sum_k \frac{\alpha_{nk}\alpha'_{km}}{E - E_k(\ldots)} + \frac{\alpha'_{nk}\alpha_{km}}{E - E_k(\ldots)}$.

puis for scattered [illegible]) : " comp. of α in dir. of polarization.

$$\alpha_{nh} = \int \psi_n^* e^{-i\underline{k}\cdot r} \alpha_p \psi_h \, dr$$

take $\psi_n = u_n e^{\frac{i}{\hbar} p_n \cdot \underline{r}}$ $\qquad \alpha_{nh} = (u_n^* \alpha u_h) \int e^{-\frac{i}{\hbar} p_n \cdot \underline{r} + \frac{i}{\hbar} p_h \cdot r - i \underline{k} \cdot \underline{r}}$

loss $\alpha_{nh} = 0$, exponent must $= 0$: $\; -p_n + p_h - \hbar k = 0$;

$\therefore$ i.e. $p_h = p_n + \hbar \underline{k}$ mom. conservation

$\alpha'_{nL} \neq 0$ only if: $p_m = p_L - \hbar \underline{k}'$;

$\therefore \underline{p}_m + \hbar \underline{k}' = p_n + \hbar \underline{k}$.

Then sum $\dfrac{(u_n^* \alpha u_h)(u_h^* \alpha' u_m)}{E_n + h\nu - E_h}$ over possible states with momentum p_L; there will be four, one for each spin, & one for $\pm$ Energy. $\therefore \sum_{\substack{\text{sign of } E \\ \text{spin of } h}}$

spin dependence sometimes interesting : neutral, retains its direction.

If not, we want sum of squares of above expression, averaged over spin of initial quantum. $\therefore \frac{1}{2} \sum_{\substack{\text{spin } m \\ \text{spin } n}} \left| \sum_{\substack{\text{sign } E \\ \text{spin } \underline{h}}} \frac{=}{-} \right|^2$. calculate sum by method of Casimir :

Now $E_h \psi_h = H \psi_h$;

plane wave : $E_h u_h = (\alpha \cdot p_L - \beta m c^2) u_h$

$$\sum \frac{(u_n^* \alpha u_h)(u_h^* \alpha' u_m)(E_n + h\nu + E_L)}{(E_n + h\nu)^2 - E_L^2}$$

$$\sum_{\substack{\text{spin of } h \\ \text{sign of } E_h}} (u_n^* \alpha (E_n + h\nu + \alpha \cdot p_L - \beta m c^2) u_h)(u_h^* \alpha' u_m)$$

$$\sum_{p_n + \hbar k}$$

$$\sum u_n^* P u_m$$

finally $\frac{1}{2} \sum_{\substack{\text{spin } n \\ \text{spin } m}} |u_n^* P u_m|^2$.

Casimir : look for operator which $= 1$ for $+$ energy, 0 for $-$ energy : it is: $\frac{1}{2}\left(1 + c\,\alpha \cdot \frac{p}{|E|} - \beta \frac{m c^2}{|E|}\right) u = \begin{cases} u & (E > 0) \\ 0 & \end{cases}$

$= \frac{1}{2}(1 + \underline{v} \cdot \alpha - \beta \mu) u = \begin{cases} 1 \\ 0 \end{cases}$.

Putting this in matrix element, will get same as before for positive energy, but 0 for negative —

$$u_n^* P (1 + v_m \cdot \alpha - \beta \mu_m) u_m = \begin{matrix} u_n^* P u_m \text{ if } E_m > 0 \\ 0 \text{ if } E_m < 0 \end{matrix}$$

$$\therefore \frac{1}{8} \sum_{\substack{\text{spin + sign of } E \\ m + n}} (u_n^* P (1 + \alpha \cdot v_m - \beta \mu_m) u_m)(u_m^* P^\dagger (1 + \alpha \cdot v_n - \beta \mu_n) u_n)$$

$$= \frac{1}{2} \; P (1 + \alpha \cdot v_m - \beta \mu_m) P^\dagger (1 + \alpha \cdot v_n - \beta \mu_n) \text{ summed over } n.$$

$I(t) = \int_0^t f(t,s)\,ds$

$I(t+\Delta t) = \int_0^{t+\Delta t} f(t+\Delta t, s)\,ds$

$\Delta I = I(t+\Delta t) - I(t) = \int_0^{t+\Delta t} f(t+\Delta t, s)\,ds - \int_0^t f(t,s)\,ds$

$= \int_0^t [f(t+\Delta t, s) - f(t,s)]\,ds + \int_t^{t+\Delta t} f(t+\Delta t, s)\,ds$

$\frac{\Delta I}{\Delta t} = \int_0^t \frac{f(t+\Delta t, s) - f(t,s)}{\Delta t}\,ds + \frac{1}{\Delta t}\int_t^{t+\Delta t} f(t+\Delta t, s)\,ds$

$\therefore \frac{dI}{dt} = \int_0^t \frac{\partial f}{\partial t}\,ds + f(t,t)$

If $\alpha = \alpha'$ (permutation [illegible]) then [illegible]

[illegible]

$\therefore$ P [illegible] for [illegible] then [illegible]

then:

$P(1+\alpha \cdot \sigma - \beta u_m)\, P^{\dagger}(1+\alpha \cdot \sigma_n - \beta u_n)$

$= A^2(1 + \sigma_m \cdot \sigma_n + u_m u_n) - 2A\,(u_m + u_n)$ [illegible]

Reading Heitler — better than Klein–Nishina original paper —
Compton scattering probability becomes greater than photo-el. effect for very high energies $\lesssim 10^5$ e.v. photo el.; $10^5 - 10^8$ Compton effect, $\gtrsim 10^8$ pair production

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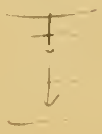
Two-quantum annihilation — positron disappears in 10^{-10} sec.



$x^\alpha p^\beta - p^\beta x^\alpha$

~~$px - xp = -i\hbar$~~

~~$xp - px = i\hbar$~~

~~$x^2p - px^2 =$~~ $xxp - xpx + xpx - pxx = x[xp] + [xp]x$

$[xp]$ $\quad [x^2p] = x[xp] + [xp]x$

$= x\, i\hbar + i\hbar\, x = 2i\hbar x$

$[xp^2] = [xp]p + p[xp]$

$= i\hbar\, p + p\, i\hbar = 2i\hbar p$

$xpp - ppx$

$xpp - pxp + pxp - ppx$

$[xp]p + p[xp]$

$[AB, C] = ABC - CAB = ABC - ACB + ACB - CAB$

$= A[BC] + [AC]B$

$[AB, C] = A[B, C] + [A, C]B$

$\Delta\psi + \frac{2m}{\hbar^2}(E - V)\psi = 0$

$[a^2, b] = a[a, b] + [a, b]a$

$[xH - Hx]$

$p \qquad \dot{q}\, H = \dot{A}_{ij} = (AH - HA)_{ij} = A_{il}H_{lj} - H_{il}A_{lj}$

$= A_{ij}E_j - A_{ij}E_i$

$= A_{ij}(E_j - E_i)$

$= -i\hbar\, \dot{A}_{ij}$

$A_{ij} = a_{ij}e^{i(E_i - E_j)t/\hbar}$

$\dot{A}_{ij} = \frac{i}{\hbar}(E_i - E_j)$

$\therefore [AH] = -i\hbar\dot{A}$

$$\sum_{mn} A_{mn} \sum_k S^{-1}_{km} S_{nk}$$

$$\sum_k S_{nk} S^{-1}_{km} = (S S^{-1})_{nm} = \delta_{nm}$$